(2.)

A MANUAL

OF

QUALITATIVE ANALYSIS.

BY

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PREFACE TO THE FIRST EDITION.

THE increased attention which has of late years been given to Chemistry in this country, has caused the production of several excellent works on Qualitative Analysis. The majority of these works have, however, been found better adapted for the advanced student than for the beginner. To supply the latter with a suitable Elementary Work is the object aimed at in the present Treatise.

The Author having had ample opportunities, for some years past, of ascertaining the difficulties which oppose the student's progress in the study of Analysis, has endeavoured in the present little Work to obviate these, as much as possible, by simplifying the course of study. The peculiar arrangement adopted, whilst simplifying the study of this particular branch of Chemical Science, will afford the student the means of increasing his knowledge of General Chemistry.

Although the Work professes to be a mere introduction

to the study of Analysis, several new processes have been
described, when they appeared to be an improvement on
those usually employed: thus, a new method is given
for the detection of magnesia, and its separation from
the fixed alkalies. The separation of phosphoric and
oxalic acids from the alkaline earths is rendered easier
or more secure to the unpractised student, by the new
process here recommended; and the determination of
tin and antimony is facilitated by a modification of the
process usually adopted. But in improving processes
which appeared to be defective, the Author has not
forgotten that the main object of the Work is to present
to the student a simple Introduction to Qualitative
Analysis.

QUEENWOOD COLLEGE,
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PREFACE TO THE SECOND EDITION.

In issuing a New Edition of this Manual, I will briefly describe in this Preface the scheme or plan of analysis developed in the Work, and the way in which the book ought to be used.

In all other works on Qualitative Analysis with which I am acquainted, the properties of the bases and acids, and the application of these properties to the analysis of substances, are treated separately. As a consequence, the student, when he goes through the experiments on each base and acid, performes these illustrations of the properties without perceiving their use or application. In the part of the Work devoted to the analytical course, he is *told what to do* either by tables (as in the "Giessen Outlines," and some other works), or, as in Fresenius, by a more tedious, and, in my opinion, as defective a method. The principles upon which these instructions are based are not given with the instructions, but in a separate Chapter of the Work;

and unless the student is able himself to unite the two—the principles with the practical instruction—he becomes a mere analytical machine. Students who can give their whole time and attention to the study of the science can, if they will, accomplish this; but I have found by experience, that those who can only devote some five or six hours in the week to the acquirement of the science, fail to become intelligent analysts by this system.

The system is very difficult, as well as defective: it is so difficult, that those who employ it generally teach one thing, useless in itself, in order that they may teach another: they teach the student first to look for one acid and one base—a limitation which is not adopted in actual practice—solely for the purpose of rendering the course in which they have to look for all the bases and acids less difficult.

In the plan I have adopted, the properties of the different members of each group are contrasted by placing them in parallel columns: the advantage of this is, that the student, after he has performed the experiments, is able himself to devise methods for the detection and separation of the different members; it places him, in fact, in the position of a judge who has to decide some cause after having heard all the

pleadings. It enables him also to judge for himself how many diffcrent methods might be adopted in the separation of substances; it therefore enlarges his views, and enables him to *reason* on the methods he adopts.

This Manual is intended to be uscd in the following way : — The studcnt commences with the first group; and after he has performed all the experiments given in the table of that group, several analyses are given him, each of which he examines for thc members of this group. When he can perform thesc practical exercises correctly, hc commences the sccond group — first pcrforming thc expcrimcnts in thc group, and then analyzing several solutions for the mcmbers of this group. When he can perform thesc correctly, he cxamincs scvcral solutions for thc mcmbers of thc first and second groups. In this progressive way hc passes through thc groups; so that by the time hc has complcted them, hc will have becomc an accuratc analyst.

In thc former Edition I proposed, and partially carried out, the division of the third group of bases, by cmploying ammonia as a group rcagcnt; this altcration not only simplifies thc subject, but it makcs thc plan of analysis taught in the laboratory morc consonant with thc methods adoptcd in actual practice. This

alteration is fully carried out in this Edition, and a more complete description of the properties of the basic groups is given.   I have also given, in this Edition, an outline of the special tests to be adopted in the detection of the acids, and considerable additions have been made in the Chapter on the Preliminary Examination of Solids.   I have also introduced a new feature —at the very commencement of the book a series of experimental exercises are given, illustrating the principles upon which analytical operations are based, which it is intended the student should perform before he commences the groups.   My aim in writing the book has been to furnish a suitable guide to the beginner; and I confidently hope that this Edition will be found superior to the former in this respect, and that it is what I wish it to be—a Student's Book.

R. G.

Dublin, *Nov.* 1857.

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QUALITATIVE ANALYSIS.

CHAPTER I.

1. QUALITATIVE ANALYSIS enables one to discover the *composition* and *properties* of any unknown substance; and it teaches one the mode of *separating* substances from each other.

2. Only those substances, which are commonly met with in nature, or which have some useful application, are treated of in this work; the following is a list of them:—

3. BASES.—Potash, soda, ammonia, baryta, strontia, lime, magnesia, oxide of manganese, oxide of zinc, oxide of nickel, oxide of cobalt, the oxides of iron, sesquioxide of chromium, alumina, oxide of uranium, oxide of lead, oxide of silver, the oxides of mercury, oxide of bismuth, oxide of copper, oxide of cadmium, oxide of gold, oxide of platinum, oxide of antimony, the oxides of tin.

4. INORGANIC ACIDS.—Arsenious acid, arsenic acid, chromic acid, carbonic acid, hydrosulphuric acid, hydrocyanic acid, sulphuric acid, boracic acid, phosphoric acid, oxalic acid, hydrofluoric

acid, silicic acid, hydrochloric acid, hydrobromic acid, hydriodic acid, nitric acid, chloric acid.

5. ORGANIC ACIDS.—Tartaric acid, citric acid, malic acid, benzoic acid, succinic acid, tannic acid, gallic acid, uric acid, acetic acid, formic acid.

6. Each of these bases and acids is A SOLID, A LIQUID, or A GAS; in whichever state it exists, it must be *soluble* or *insoluble* in water. If it is A SOLID, and *insoluble*, it will, on being separated from any of its soluble compounds, float in or upon the water or else fall to the bottom; in either case it is called a precipitate; if it is *soluble*, it will remain dissolved when separated from any of its soluble compounds. If it is A LIQUID, and *insoluble*, it will float upon the water if lighter than that liquid, and if heavier, the water will float upon it; if it is *soluble*, it will mix with the water. If it is A GAS and *insoluble*, it will, on being separated from any of its soluble or insoluble compounds, escape into the air; if it is *soluble*, it will remain dissolved in the water, if there is sufficient for its solution—if there is not sufficient, the *excess* will escape into the air; if it is dissolved by the water, it will most probably escape when the liquid is warmed, being expelled by the heat.

7. The bases, with the exception of ammonia, are all solid and non-volatile bodies. Potash, soda, ammonia, baryta, strontia, and lime, are soluble in water; the rest of the bases are insoluble in that liquid. The compound produced by the union of a base with an acid is called a salt. Many of the salts of the insoluble bases are soluble in water. The salts of the gaseous base, ammonia, and the salts of the gaseous acids, are solids; some of these solid salts are soluble, some are insoluble, in water.

8. If to a solution of any of the soluble salts of the insoluble bases a soluble base is added, the soluble base will take away the acid from the insoluble base; the latter—viz., the insoluble base —being set free, will consequently precipitate, on account of its

insolubility in the liquid. We may here observe, that many of the bases, when they are set free in this manner, *combine* with water; this compound of the base and water is termed the hydrate of the base, whichever base it may be. The three following experiments are given to teach the student the principle just stated; he must, therefore, carefully perform the experiments according to the directions:—

EXERCISES.

9. Dissolve, by the aid of heat, two or three grains of alum, which is a compound containing sulphate of alumina, in a testtube half filled with water; add ammonia to the solution after the alum is dissolved, and, after the addition, close the mouth of the test-tube with the thumb, and then shake the liquid in it very violently. If the liquid smells of ammonia *after the agitation*, a sufficient quantity has been added; but if it does not, a further quantity of ammonia must be added, and the liquid again shaken; and this must be repeated until *the liquid smells of ammonia, after it has been well shaken.* The ammonia deprives the alumina of its acid; the alumina, on being set free, combines with water —this compound of alumina and water appears under the form of a white gelatinous solid, insoluble in water.

10. Dissolve two or three grains of sulphate of copper in a test-tube half filled with water; boil the solution, by means of a spirit or gas lamp, and add to the boiling liquid a solution of caustic soda, until it turns red litmus paper blue. After the caustic soda has been thoroughly mixed with it by agitation, in the way described in the first exercise (par. 9), oxide of copper, which is of a black colour, will precipitate, owing to its being deprived of the sulphuric acid by the soda. If the oxide of copper is precipitated under the boiling point, it combines with water, forming hydrate of the oxide, which is of a blue colour.

11. Dissolve two or three grains of sulphate of zinc in a test-

tube half filled with water; add ammonia, drop by drop, until a
white precipitate, which is hydrate of zinc, is formed; then con-
tinue to add the ammonia until the precipitate disappears.   The
precipitate disappears, because the hydrate of zinc is soluble in
ammonia; it is also soluble in the other alkalies, soda and potash;
therefore, if caustic soda had been added, a precipitate would have
formed, as in the case of the ammonia, which, on a further addition
of soda, would have disappeared.

12. When substances are employed in analysis in the way
ammonia and caustic soda have been employed in the above
experiments, they are called *tests*, or *reagents*, and the phe-
nomena produced by them are termed *reactions*.   The reagents
are either acids, bases, or salts; and the reactions consist some-
times in a change of colour, sometimes in the production of effer-
vescence, but most frequently by the formation of a precipitate,
which, in many cases, possesses a characteristic colour.   Reagents
may be divided into two classes—*general* and *special*.   The
general reagents are employed to divide substances into *families*
or *groups*, and the special reagents to detect the *individual mem-
bers* of a group.   A special reagent is said to be *characteristic*,
when it produces a reaction so decisive that it admits of no
mistake.   A reagent is called *sensitive*, or *delicate*, if its action
is clearly perceptible with a very minute quantity of the substance
tested for.   The student must be very particular in always mixing
thoroughly the reagent with the solution to which he has added
it, and not simply content himself by adding it (as is generally
the case with beginners), without attempting, by *agitation*, to
incorporate the two fluids.   The way for incorporating them has
been fully described in the first experiment (par. 9): it only
remains for us to guard the student against the accident of losing
the liquid, which is likely to occur, when the liquid is hot, unless
the operator keeps his thumb firmly fixed upon the mouth of the
test-tube; because the air in the upper part of the test-tube, in

passing over the heated liquid, becomes expanded, and would therefore expel the liquid, unless the mouth of the tube was kept firmly closed.

13. If to any salt of ammonia one of the soluble bases is added, the latter will deprive the ammonia of its acid; consequently, the ammonia will be set free, which will be perceived by the smell. The soluble bases set the ammonia free from its salts in the solid state, as well as in solution; heat assists the liberation in each case. If, to any salt of the volatile acids, an acid having a stronger affinity for the base of the salt is added, the volatile acid will be set free; the decomposition takes place as well when the salt of the volatile acid is insoluble as when it is soluble, in water. The following experiments illustrate the principles here stated:—

EXERCISES.

14. Dissolve two or three grains of chloride of ammonium in a test-tube containing water; add to it some caustic soda solution, and then warm the liquid in the tube; ammonia will be set free in the gaseous state. It will be known, when it is in the *free state*, by the smell.

15. Mix two or three grains of dry powdered chloride of ammonium very intimately with a like quantity of slaked lime; place the mixture in a crucible, and warm it by means of a spirit or gas lamp; ammonia will be set free as in the previous experiment.

16. Dissolve a few grains of carbonate of soda in water; add to the solution sulphuric, hydrochloric, or nitric acid—each of these acids deprives the carbonic acid of its base: it is consequently set free; and, by its escaping through the water into the atmosphere, causes an effervescence.

17. Place a few grains of chalk or marble at the bottom of a test-tube; cover it with water, and then add to it hydrochloric or nitric acid—either of these acids deprives carbonic acid of its base, consequently it is set free; and, by its evolution, produces

effervescence, as in the previous experiment. Hydrochloric and nitric acids are to be preferred to sulphuric acid in this experiment, because the former give with lime, salts soluble in water: but the latter produces, with that base, a salt, sulphate of lime, sparingly soluble in water; the greater part of the sulphate of lime therefore falls down, and thus shields the undecomposed chalk or marble from the acid.

18. The student will see by these two courses of experiments, that salts are decomposed by adding to them either acids or bases, provided the acids or bases added have stronger affinities than the acids or bases in the existing compound; and that, according as acids or bases are added, so acids or bases are set free. Thus, ammonia and alumina are liberated from their salts on the addition of a stronger base, and carbonic acid is liberated from its combinations on the addition of a stronger acid.

19. All the salts of ammonia containing volatile acids, on being heated volatilize completely, either with or without decomposition; but the ammonia salts of the non-volatile acids— viz., phosphoric, boracic, and silicic acids—are decomposed by heat; the ammonia escapes, but the non-volatile acid remains behind. The salts of the volatile acids do not volatilize, on being heated, unless ammonia is the base; the acid may be expelled by the heat, but the base with which it was combined remains behind, with the exception of ammonia. The following experiments are given to illustrate the principles here stated:—

20. Place two or three grains of powdered chloride of ammonium in a crucible; heat the crucible, by means of a Berzelius spirit or gas lamp, until all fuming ceases. The ignition must be continued so long, because the fumes are the volatilizing salt; and therefore, until they cease, all the ammoniacal salt is not expelled. If the chloride of ammonium employed is perfectly pure, there ought to be no residue after the fuming ceases.

21. Place two or three grains of powdered chalk in a crucible;

heat the crucible for some time by means of a Berzelius spirit or gas lamp. After the lamp is removed, and the crucible has become cold, add some water to the ignited chalk, and then test the water with red litmus paper—it will change the colour of the paper from red to blue, showing that some of the carbonic acid has been expelled by the heat.

22. If to the solution of any salt an acid or a salt containing an acid is added, which acid would produce, by combining with the base of the salt in solution, an *insoluble salt*, it will always take away that base from all other acids which form with that base soluble salts, and unite with it, producing the insoluble salt; also, if to the solution of any salt a base or a salt containing a base is added, which base would produce by combining with the acid of the salt in solution an *insoluble salt*, it will always take away that acid from all other bases which form with that acid soluble salts, and unite with it, producing the *insoluble salt;* for in *whatever way* the most insoluble substances can be generated, decomposition occurs. The following experiments are given to illustrate the principles here stated:—

EXERCISES.

23. Dissolve two or three grains of nitrate of baryta in a test-tube half filled with water; add to the solution a few drops of dilute sulphuric acid; the sulphuric acid will deprive the nitric acid of the baryta, by combining with that base and forming with it an insoluble salt, sulphate of baryta.

24. Dissolve two or three grains of nitrate of baryta, as before; add to the solution a solution of sulphate of potash—sulphate of baryta and nitrate of potash will be produced. The former, being insoluble in water, will be precipitated; the latter, being soluble, will remain in solution.

25. Dissolve two or three grains of common salt, chloride of sodium, in water; add to the solution a few drops of nitrate of

silver—chloride of silver and nitrate of soda will be produced. The former, being insoluble in water, will be precipitated; the latter, being soluble, will remain in solution.

26. Dissolve two or three grains of sulphate of potash in water; add to the solution some baryta water—sulphate of baryta will be formed, and potash set free. The former, being insoluble in water, will be precipitated; the latter, being soluble, will remain in solution.

27. Before attempting to show how these different principles are employed in analysis, we must describe the principal operations employed in analysis, and give a list of the reagents and apparatus required.

OPERATIONS.

SOLUTION.

28. Many solid bodies, when placed in contact with a liquid, possess the property of becoming thoroughly incorporated with it, by passing into the fluid state. This change is expressed by the term *solution*, and the liquid in which the solid dissolves is called the *solvent*.

29. Solutions are of two kinds, *simple* and *chemical*. A *simple* or *mechanical solution* is the mere dissolving of a solid in a liquid, no chemical change occurring in either; on the removal, therefore, of the liquid by evaporation, the solid is obtained in its original condition. Common salt dissolved in water affords an illustration of a simple solution.

30. In a *chemical* solution the solid and fluid combine together, forming an entirely new substance, from which the original solid and fluid can no longer be extracted by mere mechanical operations. Chalk dissolved in hydrochloric acid affords an example of a chemical solution.

31. The solvent in a simple solution cannot dissolve unlimited quantities of the substance to be dissolved; it can only dissolve certain fixed quantities of the solid, the amount varying with the

kind of solid, and the amount of any particular solid varying with the solvent. When the solution contains as great a quantity of the solid matter as it is capable of dissolving, it is said to be *saturated*. A solution is known to be saturated when fresh solid matter of the same sort, on being put into it, remains undissolved. "But as fluids dissolve generally larger quantities of a substance the higher their temperature, the term *saturated*, as applied to simple solutions, is only relative, and refers invariably to a certain temperature." From the tendency of heat to diminish the force of cohesion, it naturally results that the solubility of most bodies is increased by heat: this, however, is not always the case; some bodies, as common salt, are equally soluble in water at all temperatures, whilst, in other cases, the solubility is greater at particular temperatures than either above or below them. The liquids employed as solvents in simple solutions are water, alcohol, ether, oils, &c. The most important solvent is water; the others are only resorted to when the substance to be dissolved is insoluble in that liquid.

32. "A chemical solution may be *accelerated* by elevation of temperature; and this is, indeed, usually the case, since heat generally promotes the action of bodies upon each other. But the *quantity* of the dissolved body remains always the same in proportion to a given quantity of the solvent, whatever may be the difference in temperature—the combining proportions of substances being invariable, and altogether independent of the gradations of temperature." The liquids which produce chemical solutions are, in most cases, either acids or alkalies.

33. The process of solution is conducted either in evaporating dishes or test-tubes. The latter are generally employed when the quantity of the solid operated upon is small. The more minutely any substance is powdered, the more its solution is facilitated. Solid substances are generally reduced to powder in mortars.

PRECIPITATION.

34. It is frequently necessary to remove a constituent—it may be either the metal or metalloid of some binary compound, or the acid or base of some ternary one—from the liquid in which the compound is dissolved. This is effected by making it a constituent of some new compound, which is insoluble in the liquid in which the original compound was dissolved. This operation, which is called precipitation, is owing, therefore, to the formation of a new solid substance, which is insoluble in the liquid in which its elements were dissolved, and which falls, or is precipitated to the bottom, owing to the solid being specifically heavier than the liquid. Occasionally, however, it is lighter, and floats upon the surface. In both cases, the insoluble substance is called the *precipitate*, and the substance producing the precipitation is termed the *precipitant*.

35. Precipitation is an operation which is constantly practised in the preparation of substances in the manufactory as well as in the laboratory. We also resort to it in the laboratory, for the purpose of detecting and separating substances from one another. Thus, if we had a solution which might contain some compound of baryta and lime: to ascertain whether baryta was present, and, if it was, to separate it from the solution, before ascertaining whether lime was likewise present, we might add a soluble chromate—if baryta was present, the chromic acid would combine with it; and as chromate of baryta is insoluble in water, it would precipitate, whilst chromate of lime, being soluble, would remain in solution. If we were now to add to the clear filtered solution some soluble oxalate, oxalate of lime, being insoluble in water, would precipitate. If the chromate produced no precipitate, there could be no baryta; if the oxalate produced no precipitate, after having separated the baryta (if present), lime must be absent.

36. Precipitates are classified, according to their appearances,

into crystalline, pulverulent, flocculent, curdy, and gelatinous. The terms *turbid* and *turbidity* are applied when the precipitate is so small that it cannot be distinguished, except by impairing the transparency of the fluid.

37. The separation of precipitates from liquids is, with some few exceptional cases, much assisted by the application of heat and agitation. The operation, when performed as an analytical operation, is conducted in test-tubes, which, from their transparency, admit of an inspection of the process.

FILTRATION AND DECANTATION.

38. These terms are applied to a modification of the same operation—viz., the mechanical separation of fluids from solid matter mixed with them.

FILTRATION.

39. In filtration, the separation of the fluid from the solid matter is accomplished by passing it through filtering paper of a proper size and shape, supported in a funnel. The pores of the paper permit the fluid to pass through; whilst the solid matter, being prevented, remains behind.

40. To prepare a filter, take a small piece of filtering paper (the best white blotting paper), and fold it twice, from side to side; then round off with scissors the projecting corners, so that the paper may fall wholly within the funnel; moisten the paper when placed within the funnel, and then carefully pour the liquid to be filtered upon it. The funnel, when large quantities have to be filtered, is supported in one of the rings of the retort stand; but in the ordinary filtrations required in qualitative analysis, it may rest on the mouth of a test-tube. The filter should not project over the edge of the funnel, especially if the substance in the filter requires to be washed. Should the first portions of the liquid which pass through the filter not be perfectly bright, which is frequently the case, they must be returned to the filter, and this

must be repeated until it is perfectly bright.   The liquid which passes through the filter is called the *filtrate*.

DECANTATION.

41. When the solid particles are very heavy, the supernatant liquid can be perfectly separated, without passing it through a filter, by simply inclining the vessel, so as to allow the fluid to pass away unattended by the precipitate, or by removing the fluid by a syphon.

42. The separation in this way of a solid from a fluid is called *decantation*.

43. Too great attention cannot be paid to the washing of pre-cipitates when they are required for further examination.   After the precipitate has been thrown upon the filter, a stream of water must be projected from the wash-bottle upon it, from time to time, until it is perfectly freed from *soluble matter;* this is sooner accomplished if hot water be employed.   Hot water may therefore be used in all cases unless the contrary be ex-pressly stated.

EVAPORATION.

44. This process is used for the purpose of obtaining matter in a solid state from solutions.   By the aid of heat, the volatile fluid passes off in the gaseous form, whilst the non-volatile matter remains behind.

45. If the evaporation be conducted slowly, the solid matter will frequently, on being deposited, assume a crystalline form. The operation is then termed *crystallization*.

46. This operation is frequently conducted for the purpose of obtaining a liquid in a more concentrated form, by volatilizing a portion only of the fluid.   Vessels are constructed expressly for the purpose, called evaporating dishes.

DISTILLATION.

47. This operation, like the former one, consists in the separation of a *volatile* from a *less volatile* fluid, or in the separation of a *liquid* from a *solid*. But in evaporation no attention is paid to the volatilized fluid, whilst in distillation it is frequently the only substance required. A distilling apparatus is therefore so constructed as to allow the evaporated fluid to be collected, which is called the *distillate*. It consists of three parts:—1, A vessel in which the liquid to be distilled is heated. 2, An apparatus in which the vapour is cooled and condensed. 3, A vessel for receiving the distillate.

48. On a small scale, glass retorts are employed; but in the distillation of large quantities, copper stills are usually substituted for them.

IGNITION.

49. By this operation volatile is separated from non-volatile solid matter; it requires the application of a high temperature, and must be conducted in crucibles. This process is therefore an *evaporation of solid bodies*.

SUBLIMATION.

50. By sublimation we effect not only the separation of volatile from less volatile solid matter, but by cooling we bring the volatile matter back to the solid state, and in this state it is called the *sublimate*.

51. This process is therefore a *distillation of solid bodies*.

FUSION.

52. This term is applied to the liquefaction of a solid, by the mere application of heat. It is also used for the decomposition of solids in the "dry way."

53. By this operation we are able to resolve insoluble substances into forms which admit of solution. This is accomplished by causing their proximate elements to unite with bodies the compounds of which will be capable of solution. Thus sulphate of baryta, which, from its insolubility both in water and acids, resists the action of reagents in the fluid state, is decomposed in this way. It is mixed with three or four times its own weight of dry carbonate of soda, and the mixed mass exposed in a crucible for some time to a high temperature. The two salts mutually suffer decomposition when placed in these conditions, the sulphuric acid passing over to the soda whilst the carbonic acid unites with the baryta. If the fused mass be treated with water, the sulphate of soda dissolves in that liquid, whilst the carbonate of baryta, being insoluble, remains behind. This substance, after being well washed, may be dissolved in hydrochloric or nitric acid. The decomposition of substances in the dry way requires, in most cases, a higher temperature than that which a small spirit lamp affords. When a limited amount of heat can only be obtained, it is better to employ a mixture of equal parts of carbonate of soda and carbonate of potash, instead of the former salt alone.

DEFLAGRATION.

54. This term is applied to all decompositions attended with noise. It also includes the oxidation of a substance by a reagent, in the dry way, on account of the slight explosions which frequently attend this kind of oxidation.

THE BLOWPIPE.

55. The mouth blowpipe is a small instrument which is employed for directing a fine and continuous stream of air into the flame of a wax candle or oil lamp. By the flame thus produced two reverse chemical operations may be performed, viz., *oxidation*

and *reduction.* The flame is therefore distinguished by these properties into the outer or *oxidizing* flame and the inner or *reducing* flame.

56. In the *oxidizing* flame, the inflammable vapour is in a state of complete combustion, being supplied and mixed with an excess of atmospheric air. From the high temperature resulting from the perfect combustion of the inflammable vapour, and likewise from the excess of oxygen, all the requisite conditions are present for causing substances with an affinity for that element to enter into union with it.

57. In the *reducing* or *deoxidizing* flame the inflammable vapour is in an incomplete state of combustion, due to a deficiency of atmospheric air : hence any metallic oxide placed in this portion of the flame is robbed of its oxygen by the inflammable vapour, which requires that element for its combustion.

58. A *reducing flame is obtained* by keeping the nozzle of the blowpipe in an inclined direction, parallel to the surface of the wick, and just touching the exterior surface of the flame. An *oxidizing flame is obtained* by keeping the nozzle of the blowpipe at the same inclination as in the former case, and introducing it into the flame to about one third the breadth of the wick, at such a distance only from the surface of the latter as to obtain a clear unbroken flame. A weak blast of air is only required for the reducing flame, but a strong blast is required for the oxidizing flame.

59. The *colour* of the reducing flame is *bright yellow* if an oil lamp or candle is used; but if gas is used, it should be of the same blue colour as the centre of the oxidizing flame. The colour of the oxidizing flame in all cases is a pale blue colour, almost invisible by daylight.

60. " When any substance is submitted to the action of the *reducing flame,* it should be so held as to be entirely surrounded by the reducing flame, and protected from the oxidizing action of

the surrounding atmosphere; but this condition being fulfilled, it should be held as near as possible to the point of the flame, in order to gain the greatest amount of heat, and prevent any deposition of soot, which would shield the substance from the action of the flame, and would be occasionally attended with other disadvantages."

61. When a substance is submitted to the action of the *oxidizing flame*, it should be held just beyond the point of this flame if a candle or oil lamp is used; but if gas is used, it should be held at a considerable distance (viz., $\frac{1}{2}$ to $\frac{3}{4}$ of an inch) beyond the point of the visible flame.*

62. " As the current of air which is supplied ought to be continuous, its production requires some attention and address. The air is not blown directly from the lungs, but is forced from the mouth by means of the cheeks. The difficulty consists in inspiring and expiring through the nose, while a continued stream escapes from the mouth. This may be attained by attention to the following directions :—Inflate the mouth fully, and then, with the lips firmly closed, and the back of the mouth closed by the tongue, breathe freely through the nostrils. While the respiration proceeds, and the mouth is inflated, allow a little air to escape through a very minute opening between the lips, renewing the supply in the mouth by occasionally admitting air from the lungs without interfering with the process of respiration through the nose."—*Parnell*. In attempting this the student will not, probably, be immediately successful, but a few days' persevering practice will enable him entirely to master this primary difficulty.

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* In order to exercise himself in the manipulation of the blowpipe flame, the student will do well to practise the reactions afforded by the oxides of manganese and copper, as described in par. 536, and the corresponding part of table on blowpipe operations.

REAGENTS.

63.—List of the reagents employed in the fluid state.

1. *Hydrochloric acid* (muriatic acid), if perfectly pure, leaves no residue when evaporated. The substances with which it is generally contaminated are iron, arsenic, and sulphuric acid.

Dilute one part of the concentrated acid with four parts of water.

Nitric acid (aqua fortis), when free from non-volatile matter, leaves no residue on evaporation. The impurities often found in it are hydrochloric and sulphuric acids.

Dilute one part of the concentrated acid with five of water.

3. *Nitrohydrochloric acid* (aqua regia) is prepared by adding four parts of concentrated hydrochloric acid to one of concentrated nitric acid.

This test is employed in an undiluted state.

4. *Sulphuric acid* (oil of vitriol) frequently contains both arsenic and lead, and not unfrequently nitrous acid. The lead is deposited to a great extent when the acid is diluted, sulphate of lead being less soluble in dilute than in concentrated sulphuric acid.

The dilute acid is prepared by adding four parts of water to every one of the concentrated acid.

5. *Tartaric acid* is generally sufficiently pure for analytical purposes. As it undergoes decomposition in solution, a small quantity only should be prepared at a time.

For use, dissolve one part, by weight, of acid, in two parts, by measure, of water.

6. *Acetic acid*, when employed in analysis, ought to be free from non-volatile matter and sulphuric acid.

Dilute one part of the acid with four parts of water.

7. *Hydrosulphuric acid* (sulphuretted hydrogen) is prepared

by adding to sulphide of iron, in an appropriate apparatus, dilute sulphuric or hydrochloric acid. The sulphuretted hydrogen is liberated in its gaseous state, and may be passed through any solution under examination; or a solution of the gas may be obtained by passing it through pure water. As this solution very soon decomposes by contact with the atmosphere, it ought to be prepared very frequently, and kept in well-stoppered bottles.

Sulphide of iron, from which hydrosulphuric acid is obtained, is prepared by projecting a mixture of thirty parts of iron filings with twenty-one of flowers of sulphur, in small portions at a time, into a red-hot crucible, replacing the cover after each addition. When the whole has been added, the ignition must be continued for a short time, until the excess of sulphur has been dissipated.

8. *Sulphurous acid* is prepared by acting upon copper or charcoal with sulphuric acid. For this purpose small pieces of charcoal are introduced into a flask, with from six to eight times their weight of sulphuric acid, and a moderate heat applied. The evolved gas must be conducted into cold water until it is no longer absorbed. On account of the great tendency which this reagent has to absorb more oxygen, and become converted into sulphuric acid, it must be preserved in well-stoppered bottles.

9. *Chlorine gas* is prepared by introducing into a flask one part of peroxide of manganese along with four parts of hydrochloric acid; the liberation of the chlorine is assisted by a gentle heat. A solution of the gas may be prepared by passing it into cold water. Chlorine water must be kept in well-stoppered bottles, and excluded from the light.

10. *Oxalic acid.*—Dissolve one part, by weight, of the acid, in twenty parts, by measure, of water.

11. *Oxalate of ammonia* must be free from sulphuric acid.

Dissolve one part, by weight, of the salt, in twenty parts, by measure, of water.

12. *Ammonia* ought to be free from non-volatile matter, and also from carbonic, sulphuric, and hydrochloric acid.

Dilute one part of the strong ammonia with four of water.

13. *Chloride of ammonium* is frequently contaminated with iron, from which it ought to be entirely free.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

14. *Sulphide of ammonium* (hydrosulphuret of ammonia) is prepared by passing hydrosulphuric acid through liquid ammonia until it no longer produces a precipitate in a solution of magnesia.

Dilute one part, with three of water.

15. *Carbonate of ammonia* must be free from non-volatile matter, and likewise from sulphuric acid.

Dissolve one part, by weight, of the salt, in four parts, by measure, of water, and add one measure of ammonia.

16. *Arseniate of ammonia* is prepared by neutralizing arsenic acid with carbonate of ammonia, and evaporating to dryness.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

Arsenic acid is prepared by dissolving arsenious acid in nitric acid, mixed with a little hydrochloric acid, evaporating the solution to dryness, and igniting somewhat below a *low* red heat, until all nitric acid is expelled.

17. *Molybdate of ammonia.*—Digest molybdic acid in ammonia until complete solution is effected; filter the colourless fluid. Solution of molybdate of ammonia, mixed with nitric acid or hydrochloric acid until the precipitate which forms at first is redissolved, must remain colourless upon boiling. If it acquires a yellow tint, the reagent contains phosphoric acid, and is unfit for use (supposing always, of course, that the hydrochloric or nitric acid was perfectly pure).

18. *Sulphate of potash.*—Dissolve one part, by weight, of the salt, in two hundred parts, by measure, of water.

19. *Ferrocyanide of potassium* (yellow prussiate of potash).— Dissolve one part, by weight, in twelve, by measure, ·of water.

20. *Ferricyanide of potassium* (red prussiate of potash).— Dissolve one part, by weight, of the salt, in twelve parts, by measure, of water.

21. *Sulphocyanide of potassium.*— Dissolve one part of the salt in ten parts of water.

22. *Chromate of potash* must be free from sulphuric acid.

Dissolve one part, by weight, in eight parts, by measure, of water.

23. *Caustic soda* is prepared by dissolving one part, by weight, of carbonate soda, in twelve parts, by measure, of water, and boiling the solution in a clean iron pan. Hydrate of lime must be added in small portions to the boiling liquid, until hydrochloric acid causes no effervescence in a portion of the liquid. When this point has been attained, the pan must be removed from the fire, and the precipitate allowed to subside. The supernatant liquid must then be drawn off by means of a syphon, or passed through a filter of bleached linen, and the filtrate evaporated rapidly over a quick fire until it has been reduced to half its original bulk. On supersaturating a portion of the liquid with hydrochloric acid, no, or only a slight, effervescence should take place. The solution must be kept in well-stoppered bottles.

24. *Carbonate of soda* must contain no sulphuric or hydrochloric acid.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of the water.

25. *Phosphate of soda* must form no precipitate with ammonia.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

26. *Acetate of soda* is made by adding acetic acid to a concentrated solution of carbonate of soda until all effervescence ceases. This solution must be free from sulphuric acid.

Dilute one part of the concentrated solution with four parts of water.

27. *Chloride of barium.*—Dissolve one part of this salt in ten parts of water.

28. *Nitrate of baryta.*—Dissolve one part of this salt in ten parts of water.

29. *Lime water* is made by digesting recently prepared hydrate of lime for some time with cold distilled water, with frequent agitation of the mixture; allow the undissolved portion of the lime to subside, decant subsequently, and keep the clear fluid in well-stoppered bottles.

30. *Chloride of calcium* is made by dissolving pure carbonate of lime in dilute hydrochloric acid: the solution thus obtained must be neutral to test-paper.

Dilute one part of the concentrated solution with five parts of water.

31. *Sulphate of lime* (gypsum).—Dissolve as much of the salt as the water will take up.

32. *Sulphate of magnesia* (Epsom salts).—Dissolve one part, in eight of water.

33. *Perchloride* (sesquichloride) of iron is prepared by dissolving recently precipitated and well washed peroxide of iron in hydrochloric acid. It must not contain any free acid.

34. *Acetate of lead.*—Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

35. *Protonitrate of mercury* is made by heating gently in a small flask nine parts of nitric acid in conjunction with ten parts of mercury, until the disengagement of nitrous fumes ceases; the solution is then boiled for some time with the undissolved portion of the mercury, care being taken to replace the water lost by evaporation. The crystals, which separate on the cooling of the liquid, are dissolved in twenty parts of cold water, slightly acidulated with nitric acid. The fluid is then filtered if neces-

sary, and the filtrate kept in a glass bottle, the bottom of which is covered with mercury.

36. *Nitrate of silver.*—Dissolve one part, by weight, of the salt, in twenty parts, by measure, of water.

37. *Nitrate of cobalt.*—Dissolve one part, in ten parts of water.

38. *Solution of indigo.*—Heat one part of indigo, in powder, with seven parts of fuming sulphuric acid. For use, dilute the solution obtained with just sufficient water to make the fluid appear of a light blue colour.

39. *Distilled water* ought always to be employed in all the above solutions and in all analytical operations. It should leave no residue on evaporation, and should give no precipitate or even turbidity with chloride of barium, nitrate of silver, oxalate of ammonia, or lime water.

40. *Reagent papers.*—Blue litmus paper serves to detect the presence of free acids in fluids, since they change the blue colour to red. Reddened litmus paper serves to detect the presence of free alkalies, and of earths and salts possessing an alkaline reaction, by changing the red colour to blue. Turmeric paper aids, like reddened litmus paper, in the detection of free alkalies, &c., by changing its yellow colour to brown.

64.—List of the Reagents employed in the dry state.

1. *Nitrate of ammonia* is made by neutralizing nitric acid with carbonate of ammonia. The solution is evaporated until crystals begin to be deposited, and is then allowed to cool. The crystals are collected and placed in well-stoppered bottles.

2. *Cyanide of potassium* must be of a milk-white colour, and perfectly free from any admixture of iron.

3. *Sulphate of iron* is principally employed for the detection of nitric acid.

4. *Copper turnings* are likewise employed for the detection of nitric acid.

5. *Carbonate of soda* must not contain any sulphuric or hydrochloric acid.

6. *Biborate of soda* (borax) is employed in blowpipe analysis. It should be heated below the fusing point to drive off its water of crystallization, and then powdered.

7. *Phosphate of soda and ammonia* (microcosmic salt) is likewise employed as a reagent in blowpipe analysis.

APPARATUS.

65. The processes employed in qualitative analysis are exceedingly simple, and do not require much apparatus for their execution. The small amount actually requisite is described in the following list, and may be procured in the shops of operative chemists.

$1\frac{1}{2}$ dozen test-tubes.
Test-tube stand.
2 small evaporating dishes.
Washing bottle.
Spirit lamp.
2 watch glasses.
Rat-tail and triangular file.
Platinum wire and foil.
Sulphuretted hydrogen apparatus.
A number of best corks.
A few lengths of small *vulcanized tubing*.

Small retort stand.
3 small glass funnels.
2 porcelain crucibles.
$\frac{1}{2}$ lb. glass tubing.
$\frac{1}{4}$ lb. glass rod.
Small mortar and pestle.
1 quire filtering paper.
Crucible tongs.
Black's blowpipe.
Tube cleaner.
2 small German beakers.
Litmus paper, blue and red.
Turmeric paper.

66. Having explained the different operations employed in analysis, we will resume our previous subject. It has been stated already, that if to a solution of any of the soluble salts of the insoluble bases a soluble base is added, the soluble base will take away the acid from the insoluble base; the latter (viz., the insoluble base) being set free, will consequently precipitate, on account of its insolubility in the liquid. If, then, we were to add the exact quantity of the soluble base required for the complete decomposition of the salt, and no more, all the soluble base we added would be combined with the acid of the original salt, and all the acid of the original salt would be combined with the soluble base —in other words, neither the acid of the salt nor the soluble base would either of them be in excess, but the entire amount of the one would be in combination with the entire amount of the other. It is impossible in practice to add the reagents with such mathematical accuracy; we are therefore obliged to add, in order to ensure the complete decomposition of a salt of this kind, the soluble base in excess: and *in this excess*, or in this *uncombined portion*, some of the insoluble bases dissolve, being soluble in the free soluble bases. One of the insoluble bases (oxide of zinc) is soluble both in the volatile and fixed alkalies; some of the others are soluble in ammonia, but insoluble in the other two; some are soluble in potash and soda, but insoluble in ammonia; others are insoluble in each of the three alkalies. And there are some, although insoluble in ammonia, are not precipitated by it, if salts of ammonia are present, and are only partly precipitated by the fixed alkalies under these circumstances.

67. The properties which the insoluble bases display, with regard to ammonia and the fixed alkalies, are exhibited in the following table, which the student must study with the aid of the experiments:—

TABLE SHOWING THE SOLUBILITY OF THE BASIC OXIDES AND THEIR HYDRATES.

NAMES.	SYMBOLS.	NAMES.	SYMBOLS.
Soluble in water.			
Hydrate of potash } *white*	KO, HO	Hydrate of baryta } *white*	BaO, HO
Hydrate of soda	NaO, HO	Hydrate of strontia	SrO, HO
		Hydrate of lime	CaO, HO

The rest are insoluble in water.

Soluble in ammonia and the fixed alkalies.

Hydrate of zinc (*white*)		ZnO, HO

Insoluble in ammonia and the fixed alkalies.

NAMES.	SYMBOLS.	NAMES.	SYMBOLS.
Hydrate of the sesquioxide of iron (*reddish brown*)	Fe_2O_3, 3HO	Protoxide of mercury (*forms no hydrate*)	HgO
Hydrate of bismuth (*white*)	BiO, HO	Hydrate of the peroxide of mercury (*yellow*)	HgO_2, HO

Insoluble in ammonia, soluble in the fixed alkalies.

NAMES.	SYMBOLS.	NAMES.	SYMBOLS.
Hydrate of alumina	Al_2O_3, 3HO	Hydrate of the sesquioxide of chromium (*bluish green*). (This oxide is insoluble in boiling solutions of the fixed alkalies)	Cr_2O_3, 3HO
Hydrate of the protoxide of tin -	SnO, HO		
Hydrate of the peroxide of tin } *white*	SnO_2, HO		
Oxide of antimony	SbO_3	Hydrate of lead (*white*). (This hydrate is only very slightly soluble in the fixed alkalies)	PbO, HO

Soluble in ammonia, insoluble in the fixed alkalies. The presence of ammoniacal salts prevents some of them from being completely precipitated by the fixed alkalies.

NAMES.	SYMBOLS.	NAMES.	SYMBOLS.
Hydrate of cobalt (*pale red*)	CoO, HO	Hydrate of copper (*whitish green*). (If the fixed alkalies are added to cold solutions of copper salts, the hydrate is precipitated; if added to boiling solutions, the anhydrous oxide is precipitated)	CuO, HO
Hydrate of nickel (*green*)	NiO, HO		
Oxide of silver (*forms no hydrate*)	Ag O		
Hydrate of cadmium (*white*)	CdO, HO		

Insoluble in ammonia and the fixed alkalies; but in the presence of salts of ammonia, the volatile alkali cannot precipitate them, and the fixed alkalies only do so in part.

NAMES.	SYMBOLS.	NAMES.	SYMBOLS.
Hydrate of magnesia (*white*)	MgO, HO	Hydrate of protoxide of iron is of a white colour, which, on exposure to the air, finally becomes red, owing to its being converted into the peroxide	FeO, HO
Hydrate of manganese (*white*), speedily becoming brown by absorbing oxygen from the air, and becoming converted into a higher oxide	MnO, HO		

Ammonia does not precipitate the hydrate from solutions of peroxide of mercury, but a white precipitate having the following composition (Hg NH_2 + Hg Cl); the fixed alkalies likewise throw down the same precipitate, if salts of ammonia are present, but in the absence of these salts they precipitate the hydrate.

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68. To a solution of sesquichloride of iron add a solution of caustic soda in excess: hydrate of the sesquioxide of iron will precipitate, and will not be redissolved by an excess of the caustic soda.

69. To a solution of sesquichloride of chromium add a *cold* solution of caustic soda, until the precipitate which first appears is redissolved; then boil the solution until the hydrate of the sesquioxide of chromium once more precipitates.

70. Add to a solution of sulphate of alumina caustic soda, until the precipitate which first forms is redissolved; then add hydrochloric acid until the solution manifests an acid reaction; and, finally, ammonia in excess, which will cause the precipitation of hydrate of alumina.

71. We will now attempt to show how the precipitation or the volatilization of one substance, and the non-precipitation or non-volatilization of another, under the same circumstances, is applied in analysis in the separation and detection of substances. Limiting our observations to the bases, we must first inquire in what state they can be precipitated.

72. The *soluble bases* can only be precipitated from their solutions in the form of salts; therefore, if we wish to precipitate a soluble base from its solutions, whether it exists in the solution uncombined or as a salt, we must add to the solution *some acid*, or some salt containing *an acid*, which acid will form with the soluble base, a salt *insoluble* in the solution from which it has to be precipitated, whether the solution be acid, alkaline, or neutral. Now, if an insoluble salt cannot be formed, in *the state the solution is in*, we must alter the properties of the solution that we may be able to effect the precipitation: for instance, if the solution is acid, and the salt of the base we wish to precipitate is soluble in acids, we must first neutralize the solution by some base, before attempting the precipitation.

73. The *insoluble bases* must, if in solution, be in the form of

salts; those of them, however, which are soluble in the volatile
or fixed alkalies, can also be present in solution, by being dissolved
in the alkalies in which they are soluble. The insoluble bases
can be precipitated from the solution of their soluble salts, either
as *insoluble salts* or in an *uncombined state;* therefore, to pre-
cipitate the insoluble bases from the solutions of their soluble
salts, we must add *some acid*, or a *salt containing an acid*, which
will form with them a salt perfectly *insoluble* in the solution;
or we must add *some soluble base* in an excess, of which the
insoluble base does not dissolve. We can precipitate them from
their *alkaline solutions* by adding a *free acid*, which forms with
them an insoluble salt; but, in the generality of cases, they
cannot be precipitated from their alkaline solutions by a *salt* the
acid of which forms with them a salt insoluble in a neutral or
acid solution, or by a *soluble base* in which they are insoluble:
before they can be precipitated from alkaline solutions either by
salts or bases, we must, in the generality of cases, *neutralize* the
alkali in which they are dissolved, by some acid. (Experiment,
par. 70.)

74. The *volatile base*, ammonia, if in the free state, is at
once distinguished by the smell; but when it is present in solu-
tion, in the form of a salt, the salt must be decomposed by
the addition of some stronger base, before the ammonia can be
detected.

75. We will now give a few examples * as illustrations.
Suppose we had to examine a liquid for baryta and lime: they
might be present in the solution either in the uncombined state or
as salts; and as chromate of baryta is insoluble, and chromate of
lime soluble, we might add to the solution a soluble chromate—
say, chromate of potash. If we obtained a precipitate by the soluble

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* The teacher ought to give the student three or four solutions on each
example; some of the solutions containing one of the substances named in the
example, some containing both of the substances named in the example.

chromate, baryta must be present; if we obtained no precipitate, it must be absent: to the filtrate from the chromate of baryta precipitate, or to the solution which has failed to give a precipitate with the soluble chromate, we must add some acid, or a salt containing an acid, which forms with lime an insoluble salt—say we add oxalic acid, or oxalate of ammonia; if either of these reagents produces a precipitate, lime is present; if it does not produce a precipitate, lime is absent.   Suppose we had to examine a solution for sesquioxide of iron and alumina: now if the sesquioxide of iron was present in the solution, the liquid could not have an alkaline reaction,* because sesquioxide of iron is insoluble both in the volatile and fixed alkalies; therefore, if the solution is alkaline, from one of the fixed alkalies, sesquioxide of iron must be absent; if the alkalinity be due to the volatile alkali, alumina, as well as sesquioxide of iron, must be absent, because alumina, as well as sesquioxide of iron, is insoluble in ammonia.   We will suppose that the solution is slightly acid, then both substances may be present; we add to the solution one of the fixed alkalies in excess—the excess will keep the alumina in solution, but the sesquioxide of iron will be precipitated and remain undissolved.   The solution must be filtered, if a precipitate is formed; and to the filtrate, or to the solution which has failed to give a precipitate, must be added hydrochloric acid in excess: if ammonia is then added in excess, alumina, if present, will be precipitated.   Suppose we had to examine a solution for ammonia and potash: as the same reagents which precipitate potash precipitate also ammonia, the latter, when present, must be got rid of before potash can be tested for; we are therefore obliged to look for ammonia first.   To ascertain if it is present, we add to a part of the solution some soluble base, as potash or soda; if present, it will be liberated from its combinations by either of these reagents, and can then be

* Unless fixed organic matter was present, which is a condition it would be improper to consider or notice at present.

detected by the smell, &c. When present, the other portion of the solution must be evaporated to dryness, and the ignition continued until all the ammoniacal salt is expelled; if, after the expulsion of the ammoniacal salt, a residue remain, it must be dissolved in water, and examined for potash by tartaric acid or bichloride of platinum.

HOW THE WORK IS TO BE STUDIED.

76. The mode of separating one substance from another, and the properties and appearances of the precipitates, are the first things to be studied in qualitative analysis. The student gains this preparatory knowledge by performing the different experiments pointed out in the *special tables*, carefully noting the reactions which the reagents give with each individual member, and explaining by diagrams the decompositions produced.

77. These remarks may be illustrated by an example. The first group, and therefore the one which first claims the attention of the student, is made up of three members, viz., POTASH, SODA, and AMMONIA. In *the first paragraph*, under the head AMMONIA, it is stated that this substance and its salts are *volatile*, i.e., they can be converted by heat into vapour. In the second paragraph it is stated that all salts of ammonia are decomposed on the addition of a stronger base, gaseous ammonia being given off. In the third, that *tartaric acid* produces, in neutral and alkaline solutions of ammonia, a white crystalline precipitate of bitartrate of ammonia. He has, therefore, to perform and verify these experiments, to notice those conditions which favour the reactions and those which prevent their development.

78. Let *bitartrate of ammonia* be taken as an example of what has just been said. It is stated in the table that this precipitate is produced both in neutral and alkaline solutions, but that free alkalies and free mineral acids dissolve it. Hence it follows, that though tartaric acid produces a precipitate in alkaline solutions,

it can do so only when it is added in excess; because, as free alkalies dissolve the precipitate, they must, when present, prevent its formation. It is also evident that tartaric acid cannot detect ammonia in the presence of free mineral acids, for the same reason.

79. The conditions which favour or prevent precipitation, together with the appearances of the precipitates, must therefore be carefully remembered by the student. This is best accomplished by recording them in a note-book at the time the experiments are made, together with diagrams of the decompositions which the different substances experience on the addition of the reagents.

80. To exemplify what we wish to convey respecting decompositions, we select chloride of ammonium, and show by a diagram the change which this salt undergoes when tartaric acid is added to it, thus :—

$$
\begin{array}{l}
\text{Tartaric Acid.}
\left\{
\begin{array}{l}
\overline{\text{T}} \\
\text{H} \\
\text{O} \\
\text{H O}
\end{array}
\right.
\qquad
\begin{array}{l}
\text{H Cl} \\
\text{Hydrochloric Acid.}
\end{array}
\\[3em]
\text{Chloride of Ammonium.}
\left\{
\begin{array}{l}
\text{NH}_4 \\
\text{Cl}
\end{array}
\right.
\qquad
\begin{array}{l}
\text{N H}_4\text{O, H O, }\overline{\text{T}} \\
\text{Bitartrate of Ammonia.}
\end{array}
\end{array}
$$
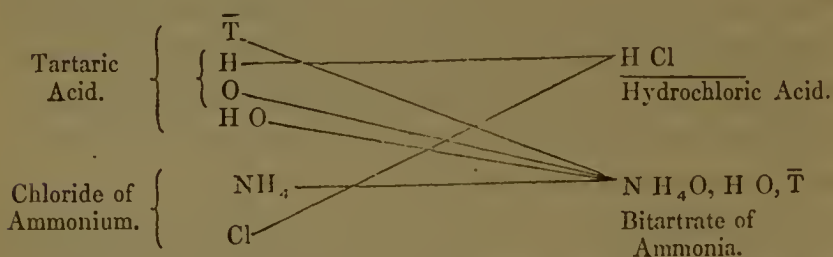
81. The student having performed all the experiments under ammonia, potash, and soda, must found upon them a method for detecting these three substances when they occur together, and then compare it with the one given in the text. By adopting this plan, a more extensive and accurate knowledge will be acquired than if the method given in the work be immediately consulted. Several solutions are then given to him, each of which he must examine for the members of this group. When he can perform these practical exercises correctly, he may pass on to the second group, performing the experiments given in

that table in the same manner. He must deduce from them the method for separating the members of this group from each other, and again test his acquired knowledge by practical exercises. When he thoroughly comprehends the way of separating them from one another, he will find, by the aid of the *general table* (chapter 3), the method to be employed for separating this group from the first. He should then examine various solutions which may contain all the members of the first two groups. When he has completed all the basic groups in the manner described, he should analyze about twenty different solutions and look for all the bases given; after which, the experiments given under the different acids must be performed. The student is then in a condition to go through a complete course of *qualitative analysis*, commencing with substances already in a state of solution, and concluding with the examination of solids. Both in the solutions and solids he must look for all the acids and bases treated of in the work.

82. SOURCES OF ERROR.—One frequent source of error with the young analyst has already been noticed, viz.: the imperfect mixture of the reagents with the solutions to which they are added. Another prolific source of error is the too liberal or the too sparing addition of the reagent, both being objectionable. To show the objectionable nature of a too sparing addition of the reagent, we will suppose the student to be examining a solution for baryta and lime; we will further suppose he has added chromate of potash and obtained a precipitate,* which proves the presence of baryta. He filters, and to the filtrate he adds oxalate of ammonia, to test for lime; he obtains a precipitate with oxalate of ammonia, although lime is absent, because he has not added

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* Whenever a precipitate is obtained, it must be separated from the fluid by *filtration*, if either the fluid or the precipitate have to be examined further; the fluid for other substances, the precipitate for the detection of the several substances which may have been precipitated, or for the confirmation of any one substance.

sufficient quantity of chromate of potash to precipitate all the baryta: thus, by the imperfect addition of a reagent, he arrives at a wrong conclusion. This fruitful source of error, viz., imperfect precipitation, may be avoided by adding to the filtrate a little more of the reagent with which the precipitation was effected. If this produces no further precipitate, the substance has been fully precipitated. Should a further precipitate be produced, it must be removed by filtration before attempting to throw down any other substance. The student must also carefully distinguish between the terms *precipitate* and *filtrate*, and be very particular in thoroughly washing the precipitates which require further examination. The wash-water must not be collected with the filtrate, if this last should be required for further examination. But all these precautions will have been attended to in vain should the experiments be performed in dirty apparatus, this being sufficient of itself to nullify all satisfactory results.

83. SYSTEMATIC COURSE OF QUALITATIVE ANALYSIS.—A qualitative investigation may be made with a twofold view, viz.—either, 1st, to prove that a certain definite body is or is not contained in a substance (*e. g.*, lime in a mineral water); or, 2nd, to ascertain all the constituents of a chemical compound or a mixture. A few simple experiments enable us to determine the first; but if we wish to discover all the constituents of a chemical compound or a mixture—if we intend to prove that, besides certain bodies which we have detected, no other substance can be present—we must know *not only the behaviour of the different substances we are to look for with the reagents* we shall employ, but we must know also *the order and succession* in which the reagents are to be applied.

84. It would be very difficult, if not impossible, to examine a solution for all the bases, if we were obliged to precipitate them singly from the solution, because it would be impossible to meet with, for each base, a reagent that would only precipitate that

base and no other. For this and other reasons we divide the bases into families or groups; the acids are also divided into groups, but their division is more imperfect than that of the bases. The separation into groups is effected by observing some property common to several substances and peculiar to them, by which means a group is formed possessing distinctive characteristics, which distinguish its members from the *lower* groups. Most important advantages are gained by a distribution of this kind, as it would be impossible to analyze complex substances accurately without some such division; for as many of the reagents precipitate more than one substance, it would be difficult to decide in such cases what the particular substances were which had been precipitated, and whether they had all been detected. Another important advantage arising from this arrangement is, that it is as easy to discover a group as an individual substance; and the absence of a group being proved, it is unnecessary to examine further for any member contained in it.

85. We have divided the bases into the following six groups:—

GROUP VI.

1*st Division.*

Oxide of Silver.
Protoxide of Mercury.
Oxide of Lead.

2*nd Division.*

Oxide of Lead.
Peroxide of Mercury.
Oxide of Bismuth.
Oxide of Cadmium.
Oxide of Copper.

GROUP V.

Arsenious Acid.
Arsenic Acid.
Oxide of Antimony.
Protoxide of Tin.
Peroxide of Tin.
Peroxide of Gold.
Peroxide of Platinum.

Group IV.

Alumina.
Sesquioxide of Chromium.
Protoxide of Iron.
Sesquioxide of Iron.

Group III.

Oxide of Zinc.
Oxide of Manganese.
Oxide of Nickel.
Oxide of Cobalt.

Group II.

1st Division.

Baryta.
Strontia.
Lime.

2nd Division.

Magnesia.

Group I.

Potash.
Soda.
Ammonia.

86. When the different substances have been divided into groups, each group is divided and subdivided, until the individual detection of the various substances present is finally accomplished.

87. Arrangement of the results of the Analysis.—The student, during the course of his analytical studies, ought invariably to record the results of each analysis in his note-book, in a systematic and tabular form. An illustration is given to show the method to be pursued.

88. Preliminary Examination of a Solid Substance.—1st, It is a colourless crystallized substance, probably a salt. 2nd, Heated alone, on charcoal, it deflagrates—a white infusible substance remaining behind, which becomes luminous, and imparts a crimson colour to the flame, probably strontia. 3rd, Soluble in water; the solution is neutral to test-paper. As it is soluble in water, a large number of substances, all the insoluble salts, must be absent; as it is neutral to test-paper, all the salts of the alkalies and alkaline earth having an alkaline reaction must be absent; and the soluble salts of the other metals, with the exception of manganese and silver, must be absent, because their soluble neutral salts redden blue litmus paper.

89. The preliminary experiments indicate the presence of nitrate of strontia.

On the addition of hydrochloric acid, no effervescence; absence of CO_2 and H S.

H Cl.	H S.	(process)	N H₄ S	N H₄ O, C O₂. A white precipitate formed.	To one portion added CaO, SO₃.	Precipitated the Sr O from the other portion, by H O, S O₃.	Divided the filtrate into two portions. — To one portion added 3 N H₄ O, As O₅.	Evaporated the other portion to dryness, to expel ammoniacal salts.
No precipitate. Absent: Ag O, Hg₂ O, and probably Pb O.	No precipitate. Absent: Hg O, Pb O, Bi O₃, Cd O, Cu O, and As O₃ As O₅ Sn O Sn O₂ Sb O₃ Pt O₂ Au O₃	Boiled to expel H S; added a few drops of H O, N O₅; again boiled; added, lastly, N H₄ Cl, and N H₄ O. No precipitate. Absent: Fe₂O₃, Al₂O₃, and Cr₂O₃. The substance being soluble in water, the phosphates and oxalates of the alkaline earths could not be present.	No precipitate. Absent: Mn O. Zn O. Ni O. Co O.	May be present. Ba O, CO₂, Sr O, CO₂, Ca O, CO₂; dissolved in H O, A̅; divided into two portions.	A precipitate, after lapse of some time, presence of Sr O, absence of Ba O.	Added to the filtered liquid N H₄ O, and H O, O̅. No precipitate. Absent: C a O.	No precipitate. Absent: M g O.	No residue. Absent: Na O, K O.

Boiled a portion of the original solution with Na O, H O. No ammonia evolved; absence of ammoniacal salts.

EXAMINATION FOR ACIDS.

90. The following acids, viz., CO_2, HS, AsO_3, AsO_5, and CrO_3, were proved to be absent on the examination for the bases.

91. The remainder of the acids, which give precipitates with a salt of baryta, could not be present; as they likewise form, with strontia, insoluble salts.

92. Added to a portion of the original solution AgO, NO_5, no precipitate; absent Cl, Cy, Br, and I.

93. Added to another portion HO, SO_3, and copper turnings, nitrous fumes were evolved, showing the presence of nitric acid.

94. The examination for chloric acid yielded a negative result.

CHAPTER II.

SPECIAL PROPERTIES OF THE BASIC GROUPS.

FIRST GROUP.

POTASH. SODA. AMMONIA.

95. The members of this group are called alkalies. They are readily soluble in water in their pure (caustic) state. The solution restores the blue colour of reddened litmus paper, and imparts an intensely brown colour to turmeric paper; the solution of their sulphides and carbonates acts in a similar manner upon vegetable colours.

96. Potash and soda are oxides of the metals *potassium* and *sodium;* these metals are lighter than water, and decompose it at the ordinary temperature. Ammonia (NH_3), being a gas of a very pungent odour, is readily distinguished from all the other bases; it dissolves freely in water, and may be again expelled on boiling the solution. Ammonia, when dissolved in an aqueous solution, unites with one atom of water forming NH_4O, the oxide of an hypothetical compound metal *ammonium* (NH_4).

97. Potash cannot be detected in the presence of ammonia or any of its salts; because the same reagents, which precipitate potash from its solutions, form also with ammonia a corresponding class of insoluble substances (A. 3. and B. 3.); the latter must therefore be *expelled* from the substance under examination, before proceeding to test for the former. The way for expelling the ammonia is described in paragraph 108.

98. How to ascertain the presence or absence of each of the three members of this group in a solution which can only contain these three bases. — As the presence of ammonia interferes, as before stated, with the detection of potash, we are always obliged, on this account, to look for ammonia before we look for potash.   And as the reagent we add, for the detection of ammonia, would interfere (A. 2.) with the detection of the two other members of the group, we are obliged, on this account, to look for the ammonia in a *portion* only of the solution under examination.   For these reasons, then, we divide the solution into two parts, which we shall call A. and B.

99. In A. we *examine* for AMMONIA according to the method described in A. 2. and paragraph 106.   The method there described is the characteristic test for ammonia; in that way it can be distinguished from all other substances.   As the absence or presence of ammonia regulates our mode of search for the two other members of the group, we must describe the mode of proceeding to be adopted when it is *absent*, as well as when it is *present*.

100. *If it is absent*, the B portion of the solution is examined for soda and potash in the following way:—A *clean* (*see* precautions, 104 paragraph) platinum wire is dipped into the solution, and then exposed to the inner blowpipe flame: if the flame is coloured *yellow*, SODA is present; if it is coloured *violet*, it proves the absence of soda (C. 4.) and the probable presence of POTASH (B. 4.).   The *presence of potash* is *discovered or confirmed* by adding to the solution under examination, which must be cold (B. 3.), a solution of *tartaric acid* in excess, and shaking the mixed liquid very violently, and then allowing it to rest for some time; if a crystalline precipitate appears after this, POTASH is present (B. 3.).   The time required for the appearance of the

crystalline precipitate depends upon the quantity of potash in the solution; if the quantity of potash is small, the precipitate may not appear until several hours after the addition of the tartaric acid solution.

101. *If ammonia is present,* the B portion of the solution must be evaporated to dryness and *ignited,* in order to volatilize the ammonia or its salts (A. 1., and paragraph 108); the ignition must be continued as long as any white fumes or smoke are evolved. If a residue remains, after the ammonia or its salts are expelled, one or both of the other two members of the group are present; this residue must be dissolved in the smallest possible quantity of water, and *examined* for POTASH and SODA, in the way described in the preceding paragraph.

102. WHEN THE EXAMINATION IS NOT CONFINED TO THE AL-KALIES, BUT ALL OR, AT LEAST, SOME OF THE OTHER BASES HAVE TO BE SOUGHT FOR IN THE SOLUTION, the solution, after being freed from all the other bases but those of the first group, must be evaporated to dryness, and ignited, to expel the ammoniacal salts, which have been added for their discovery. If a residue remain,* after the vapour of the ammoniacal salts has ceased to be evolved, it must be examined for potash and soda, in the way described in paragraph 100. In this case—that is, when other bases besides those of the first group have to be sought for—AMMONIA is to be tested for in a part of the *original solution.*

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* A fixed residue is not a certain proof of the presence of potash or soda, as it may arise from the presence of one of the non-volatile acids, viz., phosphoric, boracic, or silicic acid (*see* par. 19).

TABLE I.

Behaviour of the First Group with the Special Reagents.

Ammonia (N H$_4$ O).	Potash (K O).	Soda (Na O).
A. 1. Ammonia and its salts are *volatile*. (*See* par. 108.)	B. 1. Potash and its salts are *not volatile*.	C. 1. Soda and its salts are *not volatile*.
A. 2. All salts of ammonia are *decomposed* with the liberation of free ammonia, when any stronger base, such as *lime*,* *potash*, or *soda*, is added to their solutions. If the liquid be gently heated, the ammonia is volatilized, and its presence may then be recognized in three distinct ways. *a*, By its pungent *odour*. *β*, By turning *red* litmus paper *blue*. *γ*, By forming *white fumes*, when any volatile acid, as hydrochloric acid, is brought into contact with it.†	B. 2. When salts of potash are decomposed by a stronger base, the potash which is liberated, *not being volatile* like ammonia, cannot be detected in a similar way.	C. 2. When soda salts are decomposed by a stronger base, the soda which is liberated, *not being volatile* like ammonia, cannot be detected in a similar manner.
A. 3. *Tartaric acid* (2 H O, C$_8$H$_4$O$_{10}$ = 2 H O, T), in solution, produces in neutral or alkaline solutions of ammonia a white crystalline precipitate of Bitartrate of Ammonia (N H$_4$O, H O, $\overline{\text{T}}$), which is rather more soluble in water than the corresponding potash salt. Vigorous shaking promotes the formation of this and the corresponding potash salt.	B. 3. *Tartaric acid*, in solution, throws down from neutral or alkaline solutions of potash a white crystalline precipitate of Bitartrate of Potash (KO, HO, $\overline{\text{T}}$). This salt, and the corresponding one of ammonia, are soluble in free alkalies and free mineral acids. Slightly soluble in cold, much more so in hot, water.	C. 3. *Tartaric acid*, in solution, produces no precipitate in solutions of soda, except in *extremely* concentrated solutions, bitartrate of soda being soluble.
A. 4. Ammonia and its salts impart to the blowpipe flame *no* characteristic colour.	B. 4. Potash and its salts tinge the outer blowpipe flame VIOLET.	C. 4. Soda and its salts impart to the exterior blowpipe flame an intense YELLOW colour. Small quantities of soda can by this means be detected in the presence of much potash, the yellow flame overpowering the violet.

* If lime is employed, it must be the solid hydrate, not a solution of lime (lime water).

† This experiment is best performed by inserting a glass rod moistened with hydrochloric acid into the mouth of the test-tube in which the decomposition of the ammonia salt has been effected. The hydrochloric acid employed should not be concentrated, but should be diluted with an equal volume of water. (*Consult* par. 106.)

103. *The following precautions are to be attended to in the analysis of this group:*—In testing for ammonia, one error frequently committed is that of allowing the glass rod to remain so long in the heated atmosphere of the test-tube, that on its removal a *sensible evaporation* takes place from its surface, which is mistaken for the white fumes which are formed when any volatile acid is brought in contact with ammonia. To avoid this error, the solution which is under examination should be heated until it approaches the boiling point, but should not actually be boiled, and the moistened glass rod should, immediately after its insertion into the test-tube, be withdrawn. If any fuming should then arise, it can only proceed from the presence of ammonia, which must be confirmed by the other appropriate tests. Young students seldom continue the ignition for the expulsion of the ammoniacal salts sufficiently long; consequently they *find* potash, *when it is not present*, owing to the unexpelled ammonia giving precipitates with tartaric acid and bichloride of platinum: the attention of the student is therefore directed to par. 108. The detection of potash by tartaric acid requires, in the first place, that the solution be neutral or alkaline, not acid, and as concentrated as possible. The reagent must then be added in excess (if the fluid is alkaline the tartaric acid must be added until the solution is acid), and the fluid well agitated. The application of heat must be avoided, and time allowed for the appearance of the precipitate, as it becomes visible only after the lapse of some hours, when small quantities of potash are present. In testing for potash or soda by the blowpipe flame, it is necessary that the platinum wire should be perfectly clean. This can only be secured by directing the blowpipe flame upon it until it ceases to impart a colour; care should then be taken not to touch, even with the fingers, that end of it on which the substance is to be placed.

<center>SPECIAL REMARKS.</center>

104. AMMONIA. — This substance is a gas, transparent and colourless, of a very pungent and peculiar smell and taste.   It is instantly absorbed by water, forming the solution of the gas called *aqua ammoniæ*.   If this liquid is boiled, the gas is expelled. When organic substances containing nitrogen decay or putrefy, carbonate of ammonia is constantly produced.   The same salt is likewise formed when nitrogenized organic substances are submitted to destructive distillation.

105. When any volatile acid is brought into an atmosphere of ammonia, they unite together, forming a solid *salt :* this is the white fumes observed on testing ammonia.

106. Ammonia may be liberated from its combinations, and detected the most securely, in the following way :—The substance supposed to contain the ammoniacal salt, either in the solid state or dissolved, is mixed with an excess of hydrate of lime in a small beaker, and, if necessary, a little water.   The beaker is covered, after the mixing, with a glass plate, on the lower side of which adheres a small piece of moist turmeric or moist reddened litmus paper.

107. *Bichloride of platinum* ($Pt\ Cl_2$) produces in neutral and acid solutions of ammonia a yellow crystalline precipitate, which is a double salt of CHLORIDE OF AMMONIUM and CHLORIDE OF PLATINUM ($NH_4\ Cl,\ Pt\ Cl_2$).

108. Ammonia and its salts are distinguished from the fixed alkalies and their salts by being volatile (A. 1.).   We have already noticed that ammonia is expelled from its aqueous solution on boiling the liquid; but salts of ammonia are not volatilized unless they are ignited in the dry state, for they are not expelled from their solutions by heat with one or two exceptions, and even these could not be volatilized with advantage in this way.   Therefore, to volatilize an ammoniacal salt we must ignite

the dry substance in a crucible over a Berzelius spirit or a gas lamp, until all fuming ceases. We must continue the ignition so long because the fumes are the volatilizing salt, and therefore, until they cease, all the ammoniacal salt is not expelled.

109. POTASH.—This alkali and its hydrate, when exposed to the air, absorb moisture and carbonic acid ; the carbonate formed dissolving in the absorbed water. Almost all the salts of this base are readily soluble in water. They are colourless, provided the constituent acid be so. This alkali is an important constituent in many of our crystalline rocks; it exists there, in combination with SILICIC ACID, ALUMINA and IRON, as a double salt of SILICATE OF POTASH and SILICATE OF ALUMINA or IRON. The decay of these rocks is occasioned by the carbonic acid in the atmosphere decomposing the alkaline silicate. It is also found in the mineral kingdom as SULPHATE and NITRATE OF POTASH, the latter being *saltpetre*.

110. *Bichloride of platinum* produces, in neutral and acid solutions of potash, a yellow crystalline precipitate,* a double salt of CHLORIDE OF POTASSIUM and CHLORIDE OF PLATINUM ($KCl, Pt Cl_2$). The presence of free hydrochloric acid promotes the formation of this precipitate. It is slightly soluble in water, but wholly insoluble in alcohol. This is a very delicate test for potash or any of its compounds: the best method of applying it is to mix the solution under examination for potash with bichloride of platinum, evaporate to dryness upon a water bath, and treat the residue with alcohol; the excess of bichloride of platinum dissolves in the alcohol, colouring the solution yellow; the double salt of bichloride of platinum and chloride of potassium is

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* Bichloride of platinum gives with iodine a dark red colour; and as this colour prevents the yellow precipitate of bichloride of platinum and chloride of potassium from being distinctly seen, iodine should be removed, if present, before testing for potash by this reagent. To remove it, evaporate to dryness with *concentrated nitric acid;* dissolve the residue in water, add hydrochloric acid and bichloride of platinum, and then proceed in the usual way.

left undissolved as a yellow crystalline precipitate. The addition of bichloride of platinum should always be preceded by that of hydrochloric acid to convert the potassium into chloride, if it should not exist already in that form.

111. SODA.—This alkali and its hydrate, on exposure to the air, attract moisture and become fluid; but in absorbing carbonic acid from the air, which it does very rapidly, it again becomes solid. The salts of this base, with a few exceptions, are very soluble; the means we have of detecting it are therefore limited. It exists in the mineral kingdom as CHLORIDE (*kitchen salt*), SUL-PHATE (*Glauber's salt*), BORATE (*borax or tincal*), NITRATE, and CARBONATE. It likewise forms a constituent of many SILICEOUS MINERALS.

112. The best test for soda is the blowpipe flame, to which it imparts a yellow colour, caused by the reduction of the soda and the subsequent reoxidation of the sodium.

113. *Antimoniate of potash* (KO, SbO_5) produces, in neutral or alkaline solutions of salts of soda, a white crystalline precipitate of ANTIMONIATE OF SODA (NaO, SbO_5). In concentrated solutions the precipitate is formed immediately; but from dilute solutions it separates only after the lapse of some time. Violent agitation of the fluid promotes the separation of the precipitate. Acid solutions decompose antimoniate of potash, antimonic acid being precipitated; free acids must therefore be first neutralized with potash before this test can be applied. Antimoniate of soda is soluble in carbonate of potash; if this substance be present in the solution it must be nearly saturated with acetic acid.

114. The double compound of bichloride of platinum and chloride of sodium is soluble in alcohol and very soluble in water; therefore this reagent (bichloride of platinum) produces no insoluble compound with soda or any of its salts, either in an aqueous or alcoholic solution.

SECOND GROUP.

BARYTA. STRONTIA. LIME. MAGNESIA.

115. The members of this group are called alkaline earths. They are soluble in water in their pure (caustic) state, also as sulphides. Magnesia, however, is very sparingly soluble in water. Their solutions exhibit an alkaline reaction.

116. The metallic radicals of these oxides are *barium, strontium, calcium,* and *magnesium,* all of which decompose water at the ordinary temperature.

117. As magnesia differs so entirely from the other members of the group in its behaviour with reagents, it has not been included in the special table.

118. The group is subdivided: the first division comprising BARYTA, STRONTIA, and LIME; the second containing MAGNESIA. The members of the first subdivision are precipitated *completely* by CARBONATE OF AMMONIA, but magnesia is precipitated *only in part* by this reagent; and if any salt of ammonia, the acid of which forms no insoluble compound with magnesia, is added to the solution containing the magnesia before adding the carbonate of ammonia, the carbonate of ammonia *will not cause the least precipitate* with the magnesia. If, therefore, we add to a solution which may contain the members of the second group, chloride of ammonium and carbonate of ammonia—baryta, strontia, and lime, if they are present, will be precipitated as carbonates, whilst the magnesia will not be precipitated in the least degree. We generally add ammonia, after adding the chloride of ammonium,

but before adding the carbonate of ammonia, to render the car-·
bonate of ammonia we employ (if it is not) a neutral car-
bonate.

119. When the student examines a solution even for the members
of this group *only*, he must precipitate the baryta, strontia, and
lime, by carbonate of ammonia, and precede the addition of this
reagent by chloride of ammoninm and ammonia.

FIRST DIVISION.

120. The precipitate produced by the general reagent, car-
bonate of ammonia, must be dissolved in acetic acid, and the
solution divided into two parts, which we shall call A and B.

121. Before we describe the way for separating the members
of this division of the group, we shall propose six questions,
which the student ought to solve by the aid of the table before
he attempts the detection of baryta, strontia, and lime. 1st, Why
are the precipitated carbonates directed to be dissolved in acetic
acid; why not dissolve them in hydrochloric acid or nitric acid?
2nd, By what single reagent can we discover, in one operation,
the absence of baryta and strontia? 3rd, How can lime be
detected in the absence of the other two members? 4th, How
can strontia be detected in the absence of baryta? 5th, How
can lime be detected when strontia is present? 6th, How can
strontia and lime be detected when baryta is present?

TABLE II.

Behaviour of the Second Group with the Special Reagents.

Baryta (Ba O).	Strontia (Sr O).	Lime (Ca O).
D. 1. *Sulphate of lime* (Ca O, S O_3), in solution, precipitates baryta *immediately* from its solutions, in the form of Sulphate (Ba O, S O_3), insoluble in acids and alkalies.	E. 1. *Sulphate of lime*, in solution, precipitates strontia *after* the *lapse of some time* from its solutions, in the form of Sulphate (SrO, S O_3), almost absolutely insoluble in acids and alkalies.	F. 1. *Sulphate of lime* produces no precipitate in solutions of lime.
D. 2. *Chromate of potash* (K O, Cr O_3), in solution, produces, in neutral and alkaline solutions of baryta, a pale yellow precipitate of Chromate of Baryta (Ba O, Cr O $_3$), insoluble in the alkalies and acetic acid, soluble in hydrochloric and nitric acids.	E. 2. *Chromate of potash*, in solution, causes in concentrated solutions of salts of strontia a bright yellow precipitate (Sr O, Cr O $_3$), but not in dilute solutions, or such as contain free acetic acid.	F. 2. *Chromate of potash*, in solution, produces no precipitate in solutions of lime, Chromate of Lime being soluble.
D. 3. *Sulphuric acid* and *the soluble sulphates* behave in the same manner in solutions of baryta as sulphate of lime.	E. 3. *Sulphuric acid* and the *soluble sulphates* precipitate strontia completely from its solutions, in the form of Sulphate. The precipitate will not appear immediately, unless the solution be very concentrated.	F. 3. *Sulphuric acid* and the *alkaline sulphates* cause only in concentrated solutions of lime a partial precipitate of Sulphate of Lime, which redissolves completely in a large amount of water.
D. 4. *Oxalic acid* (H O, $C_2 O_3$ = H O, $\overline{O}$), in solution, produces only in concentrated solutions of baryta a white precipitate of Oxalate of Baryta (Ba O, $\overline{O}$), soluble in acids. The addition of ammonia renders this reaction therefore more susceptible.	E. 4. *Oxalic acid*, in solution, precipitates, even from dilute solutions of strontia, a white precipitate of Oxalate of Strontia. The addition of ammonia promotes the formation of the precipitate.	F. 4. *Oxalic acid*, in solution, throws down from neutral solutions of lime, even if highly diluted, a precipitate of Oxalate of Lime. The addition of ammonia renders this reaction more delicate.

122. SULPHATE OF LIME precipitates baryta *immediately*, strontia *after the lapse of some time*, and lime *not at all* (*see* D. 1., E. 1., and F. 1.). One of three cases will therefore occur on the addition of sulphate of lime to the A. portion—either there will be no precipitate, or there will be one after the lapse of some time, or there will be an immediate one. If there is no precipitate, examine according to 123; if there is one after the lapse of some time, examine according to 124; if there is one immediately, examine according to 125.

123. If, in the A. portion, a solution of *sulphate of lime* causes no precipitate, even after the lapse of some time, BARYTA and STRONTIA *are absent;* LIME must therefore be present *—as one of the members of a group must, at least, be present whenever a precipitate is obtained by the general reagent of that group. † As lime, in the form of sulphate, has been added to the A. portion of the solution, we cannot in that portion discover whether it (lime) was originally present ; we must therefore confirm its presence by adding to the B. portion ammonia and a solution of oxalate of ammonia (F. 4.).

124. If, in the A. portion, a solution of *sulphate of lime* produces a precipitate after the lapse of some time, BARYTA *is absent,* STRONTIA *is,* and LIME *may be, present.* The presence or absence of lime cannot be determined, as long as any strontia remains in solution, because the reagents, which precipitate lime, precipitate strontia also. We add, therefore, to the B. portion, *dilute sulphuric acid;* this acid precipitates all the strontia (E. 3.), and only a small portion of lime in a concentrated and none at all from a dilute solution (F. 3.); in any case, sufficient lime remains in solution for detection. Filter off from the precipitate produced by the

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* If the previous group or groups have been fully precipitated before adding the carbonate of ammonia, or else they might—that is, the portion not precipitated—cause a precipitate with carbonate of ammonia.

† This statement must be read in the light of the above note.

sulphuric acid, after sufficient time (one or two hours) has been allowed for the precipitation of the sulphate of strontia, and add to the filtrate *ammonia* and *oxalate* of *ammonia*, which will cause a precipitate, if LIME is present.

125. If, in the A. portion, a solution of *sulphate of lime* causes an immediate precipitate, BARYTA *is*, and STRONTIA and LIME *may be, present*. As sulphate of lime cannot be employed to detect strontia in the presence of baryta, and as baryta causes a precipitate with all the reagents which precipitate strontia and lime, the former must be got rid of before we can ascertain the absence or presence of the two latter substances. For this purpose, *chromate of potash* must be added to the B. portion, as this reagent precipitates baryta only (D. 2., E. 2., F. 2.). To the filtrate from this precipitate (the filtrate will be of a yellow colour, from the excess of chromate of potash, if the baryta has been completely precipitated) add *ammonia* and *oxalate of ammonia*, and warm the solution; if a *precipitate is produced*, it may be due to the presence both of STRONTIA and LIME (E. 4., F. 4.); if *no precipitate is produced*, STRONTIA and LIME *are absent*. Dissolve the oxalate precipitate, if one has been produced, in as small a quantity of *dilute hydrochloric acid* as possible; then add a small quantity of the dilute solution of *sulphate of potash;* * if this reagent produces a precipitate after the lapse of some time, STRONTIA is *present*. If sulphate of potash has produced a precipitate, add some dilute sulphuric acid to complete the precipitation, and allow sufficient time (one or two hours) for the complete separation of the sulphate of strontia before filtering; add to the filtrate—or to the solution, without filtering, if sulphate of potash has produced no precipitate—*ammonia in excess;* if this last reagent produces a precipitate, LIME is present.

126. *The following precautions are to be attended to in the analysis of this group:*—The solution of sulphate of lime must

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* Care must be taken to have this reagent of the proper dilution.

always be added in the cold, as this reagent is less soluble in hot than cold water. Time must be allowed for the formation of the precipitate produced by this reagent in solutions of strontia, the formation of which is much promoted by agitation. In separating strontia from a solution by sulphate of potash, the liquid ought not to be filtered immediately, but a due time allowed for the complete separation of the precipitate from the solution; and the solution ought not to be warmed, owing to the less solubility of sulphate of lime in hot than cold water.

SPECIAL REMARKS.

127. BARYTA.—This oxide is of a greyish white colour; it combines with water, forming a hydrate (Ba O, HO). Both the oxide and its hydrate are soluble in water. The solution reacts strongly alkaline, and when exposed to the air absorbs carbonic acid and becomes covered with a film of carbonate of baryta, the absorption continuing until all the baryta has been precipitated as carbonate.

128. The salts of baryta are colourless, provided the constituent acid be so. Most of them are insoluble in water; but they are all, with the exception of the sulphate, soluble in hydrochloric and nitric acid. The salts which are soluble in water do not affect vegetable colours, and are decomposed upon ignition, with the exception of chloride of barium. The SULPHATE (*heavy spar*) and the CARBONATE (*witherite*) are the principal minerals of this oxide.

129. *Hydrofluosilicic acid* (HF, Si F$_2$) throws down, both from neutral and alkaline solutions of baryta, a white precipitate of SILICOFLUORIDE OF BARIUM (Ba F, Si F$_2$) which appears only after much agitation and lapse of some time, in dilute solutions; it is perceptibly soluble in hydrochloric and in nitric acid. Addition of an equal volume of alcohol renders the precipitation rapid, and so complete that the filtrate remains clear upon addition of sulphuric acid.

130. *Salts of baryta,* strongly heated on a thin platinum wire in the inner blowpipe flame, impart a light green colour to the outer flame; insoluble compounds should be moistened with a little dilute hydrochloric acid before applying the test. " The presence of strontia converts the colour-flame into an impure yellow colour, somewhat resembling that produced by soda. If a mixture of equal parts of carbonate of soda and chloride of barium is exposed before the blowpipe on a loop of platinum wire, the yellow flame derived from the soda will only prevail for a few minutes, and will then give place to the pale green flame of baryta, the whole of the soda being volatilized under the form of chloride of sodium."—*Chapman.*

131. Strontia.—This oxide and its salts resemble, in their colour, solubility, and other properties, the corresponding compounds of baryta. The hydrate of this oxide is however less soluble in water than the hydrate of baryta. The sulphate (*celestine*) and the carbonate (*strontianite*) are the principal minerals of strontia.

132. *Hydrofluosilicic acid* causes no precipitate in solutions of strontia.

133. The chloride and nitrate of strontia are soluble in alcohol; the corresponding salts of baryta are insoluble. If an alcoholic solution of either of these strontian salts be ignited, it will burn with a *beautiful crimson flame,* which becomes more apparent on stirring the solution.

134. Salts of strontia, when heated on the platinum wire in the inner blowpipe flame, impart a *crimson colour* to the outer flame. Insoluble compounds should be moistened with a little dilute hydrochloric acid before applying the test. The presence of baryta interferes with the test (par. 130). " A mixture of chloride of strontium and carbonate of soda will give, after a well continued blast, the characteristic crimson flame of the former."—*Chapman.*

135. Lime.—This oxide and its salts resemble in their general behaviour the corresponding compounds of baryta and strontia.

The hydrate of lime is less soluble in water than the hydrates of strontia or baryta; it is also more sparingly soluble in hot than cold water. The solution absorbs carbonic acid from the air, the lime becoming converted into carbonate. The principal minerals of lime are the SULPHATE (*gypsum, selenite* Ca O, S O$_3$+2 aq) and (*anhydrite* Ca O, S O$_3$), the CARBONATE (*chalk, limestone, calcareous spar*), the double CARBONATE OF LIME and MAGNESIA (*dolomite*) (Ca O, C O$_2$) + 3 (Mg O, C O$_2$), and the FLUORIDE OF CALCIUM (*fluor spar* Ca F).

136. *Hydrofluosilicic* does not precipitate lime from its solutions.

137. CHLORIDE OF CALCIUM and NITRATE OF LIME are soluble in alcohol. The alcoholic solution of these salts, when ignited, burns with a *yellowish red-coloured flame*.

138. *Arsenite of ammonia* produces, in aqueous solutions of chloride of calcium, an immediate precipitate of ARSENITE OF LIME. In solutions of chloride of barium or strontium a precipitate is produced by this reagent only after the lapse of some time. Should this test be resorted to for confirming the presence of lime, ammoniacal salts (if present) must first of all be removed from the solution, because all the salts of arsenious acid which are insoluble in water dissolve in it if ammoniacal salts are present.

139. Salts of lime, when heated on the platinum wire in the inner blowpipe flame, impart an orange-red colour to the outer flame; insoluble compounds of lime ought first to be moistened with dilute hydrochloric acid.

140. MAGNESIA.—This oxide differs from the other members of this group, not only by its non-precipitation by *carbonate of ammonia* in the presence of *ammoniacal salts*, but likewise from the difficult solubility of its hydrate and the ready solubility of its sulphate. The oxalate and chromate, as well as some other salts of magnesia, are soluble in water. The soluble magnesian salts have a nauseous bitter taste; they do not alter vegetable colours when in a neutral state, and, with the exception of sul-

phate of magnesia, they undergo decomposition when ignited. All the salts of magnesia which are insoluble in water dissolve readily in hydrochloric acid. Magnesia is found in the mineral kingdom principally in the state of SULPHATE (*epsom salts* MgO, $SO_3 +$ $HO + 6$ aq.), of CARBONATE, and in combination with SILICIC ACID in various proportions, forming the *meerschaum, serpentine*, &c.

141. *Ammonia* precipitates from aqueous solutions of salts of magnesia, a portion as HYDRATE (MgO, HO). The rest of the magnesia remains in solution, with the salt of ammonia formed, as a double salt. The presence of salts of ammonia prevents the precipitation altogether.

142. The *fixed alkalies* and the other *alkaline earths* precipitate magnesia from its solutions in the form of HYDRATE. This precipitate is soluble in salts of ammonia ; the addition therefore of these substances, either before or after the precipitation, prevents or redissolves the precipitate formed.

143. *Arseniate of ammonia* ($3 NH_4O$, AsO_5) produces, in solutions of magnesia, a white precipitate of ARSENIATE OF MAGNESIA and AMMONIA ($2 MgO$, NH_4O, AsO_5), which is soluble in acetic and other weak acids.

144. *Phosphate of soda* ($2 NaO$, HO, PO_5) produces, in concentrated solution of magnesia, a precipitate of PHOSPHATE OF MAGNESIA ($2 MgO$, HO, PO_5). A more insoluble magnesian salt may be produced by adding along with the *phosphate of soda, chloride of ammonium and ammonia :* the precipitate in this case being PHOSPHATE OF MAGNESIA AND AMMONIA ($2 MgO$, NH_4O, PO_5), which is soluble in free acids.

145. Phosphate of magnesia and ammonia, and arseniate of magnesia, are the only magnesian salts which are insoluble in aqueous solutions containing salts of ammonia.

146. If magnesia or any of its compounds, after being ignited strongly by the blowpipe flame upon a charcoal support, be moistened with *nitrate of cobalt*, and again ignited, the mass assumes, on cooling, a *pale flesh colour.*

THIRD GROUP.

Oxide of Zinc. Oxide of Manganese. Oxide of Nickel. Oxide of Cobalt.

147. The members of this group are insoluble in water; but they dissolve readily in the dilute mineral acids, sulphuric, nitric, and hydrochloric acids, the salts they form with these acids being soluble. They are not precipitated in the least degree from their solutions by hydrosulphuric acid, if a free mineral acid is present. They are not precipitated completely from their neutral solutions by hydrosulphuric acid, but they are completely precipitated by that acid from their alkaline solutions in the state of sulphides. Their sulphides are insoluble in the alkalies and alkaline sulphides, with the exception of sulphide of nickel, which, under certain circumstances, dissolves to a slight extent in the alkaline sulphides, imparting thereby to the solution a brownish colour.

148. The metallic radicals of these oxides possess the following properties : *manganese* decomposes water at 212 F., and *zinc*, *nickel* and *cobalt*, decompose it at a red heat, and at common temperatures in contact with strong acids.

149. The precipitate produced by the general reagent, sulphide of ammonium, after being well washed with water containing a little sulphide of ammonium,* must be examined in the following way:—If it is of a *light colour*, NICKEL and COBALT must be absent (I. 1, K. 1.). Examine the precipitate for MANGANESE by the blowpipe test (154); if manganese is *absent*, examine the precipitate for ZINC by the blowpipe test (157). When manganese is present, dissolve the precipitate in *dilute hydrochloric acid;* boil to expel sulphuretted hydrogen, then add *carbonate of ammonia* in

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* Sulphide of ammonium is added in order to prevent the precipitate from oxidizing.

excess, and boil for some time : the manganese will be precipi-
tated as carbonate (G. 3.), whilst ZINC, if present, will remain
in solution. Filter, and to the filtrate add *sulphide of ammo-
nium*—when zinc, if present, will be precipitated as sulphide;
confirm its presence by examining the precipitate by the blowpipe
test.

150. If the precipitate is *black*, all the members of the group
must be sought for. Examine the precipitate for MANGANESE by
the blowpipe test. Treat the precipitate, whether manganese is
present or not, with *cold dilute hydrochloric acid;* the sulphides of
nickel and cobalt will remain undissolved, whilst the sulphides of
manganese and zinc will dissolve. Examine the hydrochloric acid
solution for MANGANESE and ZINC, as directed in par. 149; after
having washed the black residue, examine it for nickel and cobalt
in the following way:—Expose a small portion of the precipitate
on a bead of borax to the outer blowpipe flame, in the way
directed in par. 162. A blue bead denotes the presence of cobalt;
this is a safe and certain test for cobalt; consequently, if a blue
bead is not produced, cobalt is absent. If a yellow, and not a
blue, bead has been formed, which becomes grey and dull in the
inner flame, nickel is present. When cobalt is present, nickel is
sought for in the following way:—The remainder of the precipi-
tate is dissolved in nitrohydrochloric acid, and the acid solution
evaporated almost to dryness; a concentrated solution of cyanide
of potassium is then added in excess, and the whole solution must
then be boiled for some time, adding a little water from time to
time, to replace that which is evaporated. To the solution, which
must not be filtered even if a precipitate has been formed, is added,
when it is cold, sulphuric acid slightly in excess: if in some hours
after the acid has been added a precipitate appears, nickel is
present; if no precipitate appears, or at least only a crystalline one
which redissolves in water, nickel is absent.

TABLE III.

Behaviour of the Third Group with the Special Reagents.

XIDE OF MANGANESE (Mn O).	OXIDE OF ZINC (Zn O).	OXIDE OF COBALT (Co O).	OXIDE OF NICKE (Ni O).
G. 1. Sulphide of Manganese (Mn S) is *flesh-coloured*, but becomes *own* on exposure to e air. It is soluble in the weak acids as etic, as well as in the ute mineral acids.	H. 1. Sulphide of Zinc (Zn S), like the oxide, is white. It is insoluble in acetic acid, but dissolves in the dilute mineral acids.	I. 1. Sulphide of Cobalt (Co S) is *black*. It is insoluble in the dilute mineral acids, as well as in the weaker acids. It is soluble in Nitrohydrochloric acid.	K. 1. Sulphide Nickel (Ni S) is *bla* It is insoluble in t dilute mineral aci as well as in t weaker acids. It soluble in Nitroh drochloric acid.
2. The *fixed alkalies* precipitate from sotions of this Oxide (Mn O) the HYDRATE, ich is of a whitish our at first, but speedbecomes blackish own on exposure to e air. The Hydrate *insoluble in an excess* either of the fixed al- ies. The presence of moniacal salts pres ts in a great mease the precipitation.	H. 2. The *fixed alkalies* precipitate from solutions of this oxide (Zn O) the HYDRATE, which is white. *The Hydrate of this oxide is completely soluble in an excess of either of the fixed alkalies, if it (the alkali) is perfectly free from carbonic acid.*	I. 2. The *fixed alkalies* produce in solutions of this oxide (Co O) *blue* precipitates of *basic salts of Cobalt*, which turn *green* on exposure to the air; and are converted, upon boiling, into the PALE RED HYDRATE of this oxide, which is generally discoloured, owing to a little $Co_2 O_3$ being formed. *Each of these precipitates is insoluble in an excess of either of the fixed alkalies.*	K. 2. The *fixed* kalies precipitate fr solutions of this oxi (Ni O) the HYDRA in the form of a *li green precipita* which is unalterab in the air, and *in* luble in an excess either of the fixed kalies.
3. *Carbonate of* mmonia produces in utions of this Oxide recipitate of the *Curate* (Mn O, CO_2), ich is white, *and oluble in an excess of reagent*, especially boiling.	H. 3. *Carbonate of Ammonia* produces in solutions of this oxide a precipitate of *white* BASIC CARBONATE OF ZINC, which is easily soluble in an excess of the reagent.	I. 3. *Carbonate of Ammonia* produces in solutions of this oxide a *red* precipitate of CARBONATE OF COBALT, which is *readily soluble in an excess of the reagent*, the solution having a red colour.	K. 3. *Carbonate Ammonia* produces solutions of this oxi an *apple-green* pre pitate of *Carbonate Nickel*, which is *re dily soluble in an exce of the reagent*, the s lution having a gree ish blue colour.

The alkalies fail to precipitate the members of this group in the presence of non olatile organic matter, such as starch, sugar, tartaric acid, &c.

151. *The following precautions are to be attended to in the analysis of this group:*—When manganese is present, care must be taken to expel all the sulphuretted hydrogen from the hydrochloric acid solution, before carbonate of ammonia is added to separate the manganese from the zinc. Before adding sulphuric acid to the cyanide of potassium solution, it will be better to add a little water, in order to prevent any sulphate of potash from crystallizing out, which might mislead the student as regards nickel. Frequently a small quantity of the sulphides of nickel and cobalt is dissolved by the dilute hydrochloric acid: a black but very scanty precipitate is produced, from this cause, by the sulphide of ammonium, in testing for zinc.

<center>SPECIAL REMARKS.</center>

152. PROTOXIDE OF MANGANESE.—Numerous oxides of manganese exist as natural productions, and a still larger number can be formed artificially. The only one treated of in this work is the first or lowest compound of oxygen with manganese. All the others are reduced to this state by adding to their solutions hydrosulphuric acid, or any other reducing agent. This oxide is of a greenish grey colour, and its hydrate is white. Both, however, turn brown when exposed to the air, being converted into higher oxides. Its salts are colourless or of a pale red; the solutions of those soluble in water do not affect vegetable colours; and the salts soluble in water are readily decomposed at a red heat, with the exception of the sulphate. The most abundant source of manganese is the PEROXIDE (MnO_2), which exists in nature under a variety of forms.

153. Ammonia precipitates this oxide (MnO) in part from its solutions as hydrate, which an excess of the reagent does not redissolve. But ammonia in the presence of chloride of ammonium, or in fact any salt of ammonia, the acid of which causes no insoluble compound with manganese, causes no precipitate in solutions of manganese. An ammoniacal solution of manganese

attracts oxygen from the air, which converts the manganese oxide into a higher oxide; and this latter oxide, being insoluble in ammonia, is deposited, as it becomes formed, in brownish flocks.

154. The smallest quantity of manganese can be detected in any of its compounds, by fusing them, in conjunction with carbonate of soda and a small quantity of nitrate of potash, upon platinum foil or wire, in the outer blowpipe flame ; manganate of soda (NaO, MnO_3), which is of a bluish green colour, being produced. " This method fails to detect manganese in limestone rocks, on account of the insolubility of the lime salt in carbonate of soda and nitrate of potash; but if along with the two reagents just mentioned a little borax be added, so as to attack and dissolve a portion of the mass, the well known greenish blue enamel is quickly produced."—*Chapman.*

155. OXIDE OF ZINC.—The colour of this oxide is white, but becomes yellow on being heated, regaining its original colour on cooling. The salts of zinc are colourless. The neutral ones, which are soluble in water, redden litmus paper and are decomposed by heat. The principal minerals of this metal are the anhydrous CARBONATE (calamine ZnO, CO_2) and the SULPHIDE (Zinc blende ZnS).

156. When compounds of zinc, mixed with carbonate of soda, are subjected upon a charcoal support to the inner blowpipe flame, metallic zinc is produced, which volatilizes, and, on passing through the oxidizing flame, becomes again converted into oxide. The charcoal support becomes encrusted with this oxide, which is of a yellow colour while hot, and turns white on cooling.

157. If a compound of zinc be moistened with protonitrate of cobalt and exposed on charcoal to the outer blowpipe flame, a mass of a beautiful green colour will be produced; the colour is best seen when the mass has become cold.

158. OXIDE OF COBALT.—The colour of this oxide is greenish grey, its hydrate being pale red. Salts of cobalt are red when

they contain water of crystallization, in the anhydrous state they are blue. Their solutions are red; yet when concentrated, or when they contain a free acid, they are blue or green, but they become green simply by the addition of water. The solutions of the neutral salts that are soluble in water redden litmus paper, and are decomposed by heat. The principal mineral of this metal is the BRIGHT WHITE COBALT ($Co As_2 + Co S_2$).

159. Ammonia produces in solutions of this oxide the same precipitate as the fixed alkalies do; but the precipitate is soluble in an excess of ammonia, the ammoniacal solution having a reddish brown colour: the fixed alkalies produce no precipitate, or at least a very slight one, in an ammoniacal solution of pro-toxide of cobalt. Ammonia fails to precipitate oxide of cobalt from its solutions, if chloride of ammonium is present.

160. " Cyanide of potassium ($K C_2 N = K Cy$) precipitates from *acid* solutions of cobalt salts a brownish white cyanide of cobalt, $Co Cy$, dissolving easily in an excess of the precipitant: from which solution the cyanide of cobalt cannot be again preci-pitated by acids, as it exists now in the form of cobalticyanide of potassium, $K_3 Co_2 Cy_6$.

$$2 Co Cy + 3 K Cy + H Cy = K_3 Co_2 Cy_6 + H.$$

161. "If the salt of cobalt contains nickel, the addition of hydrochloric acid to the solution of the cyanides produces a greenish precipitate, which always contains the whole of the nickel, and under particular circumstances all the cobalt—that is, when these two metals are in the proportion of three equivalents of nickel to two equivalents of cobalt. The precipitate consists then of cobalticyanide of nickel, $Ni_3 Co_2 Cy_6$. In case of a larger proportion of nickel, the precipitated cyanide of nickel is mixed with the former compound; but if the proportion of nickel is smaller, a part of the cobalt remains in solution as cobalticyanide of potassium."—*Will*.

162. The compounds of cobalt fused with borax in the loop of a platinum wire, in either flame of the blowpipe, produce a beautiful blue glass, which is a very delicate and characteristic test for cobalt. The cobalt compound must be used in very small proportion.

163. OXIDE OF NICKEL.—The colour of this oxide is grey, its hydrate is green. Its salts likewise exhibit this latter colour, except when anhydrous; in this state they are mostly yellow. The solutions of the neutral salts, which are soluble in water, redden litmus paper, and are decomposed at a red heat.   The principal minerals of this metal are the ARSENICAL NICKEL (Ni As) and the NICKEL GLANCE (Ni S$_2$ + Ni As$_2$).

164. Ammonia, added in small quantity to solutions of this oxide, produces in them a trifling greenish turbidity; upon further addition of the reagent, this redissolves readily to a blue fluid, containing a compound of oxide of nickel and ammonia.

165. Cyanide of potassium throws down from solutions of nickel a yellowish green precipitate of cyanide of nickel (Ni Cy), which redissolves in an excess of the precipitant as a double salt of cyanide of nickel and cyanide of potassium (Ni Cy + K Cy); the solution is brownish yellow.   On the addition of hydrochloric or sulphuric acid to a solution of this double salt, the cyanide of nickel is reprecipitated, whilst the cyanide of potassium is decomposed, hydrocyanic acid being evolved; the cyanide of nickel is very difficultly soluble in an excess of either of the acids in the cold, but more readily upon boiling.

166. In the exterior flame of the blowpipe, oxide of nickel and its compounds impart to beads of borax a reddish yellow tint; the colour fades upon cooling, and finally disappears almost entirely.   If exposed with borax to the inner flame, the bead becomes grey; if a minute fragment of nitrate of potash be added to the bead after exposure to the inner flame, and it is then fused in the outer flame, it acquires a rich purple colour.

FOURTH GROUP.

ALUMINA.   SESQUIOXIDE OF CHROMIUM.   SESQUIOXIDE OF IRON.
PROTOXIDE OF IRON.

167. The members of this group are insoluble in water, but they dissolve readily in the dilute mineral acids; after ignition, however, they dissolve with great difficulty, even in the concentrated mineral acids.

168. The metallic radicals of these oxides decompose water at a red heat, and at common temperatures in contact with strong acids.

169. Sulphide of ammonium precipitates the members of this group: it precipitates alumina and sesquioxide of chromium as oxides, for sulphide of aluminum and sulphide of chromium cannot be formed in the humid way; they (the sulphides) are decomposed by water into the oxides of the metals and hydrosulphuric acid. It is, therefore, the ammonia in the sulphide of ammonium which determines the precipitation of these two substances; consequently hydrosulphuric acid is always evolved when sulphide of ammonium is added to a solution containing either or both these substances.   Protosulphide of iron is always formed when sulphide of ammonium is added either to a solution of a per- or proto- salt of iron, as a persulphide of iron is not formed in the humid way. Protosulphide of iron is of a black colour; it oxidizes rapidly on exposure to the air, which causes its colour to change from black to brown.

170. The precipitate produced by the general reagent, ammonia, after being well washed to free it from all foreign substances, must be examined in the following way:—

171. 1st. Manganese precipitates in small quantities along with the members of this group, owing to its becoming converted into a higher oxide, the cause of which is fully explained at (153). A small portion of the washed precipitate must be examined for MANGANESE by the *blowpipe test* (154).

172. 2nd. Another portion of the washed precipitate must be dissolved in as small a quantity of dilute *hydrochloric acid* as possible: to this acid solution a cold solution of *soda* or *potash* in excess must be added, which will precipitate IRON as peroxide (N. 3.), if present; the presence of iron must be confirmed by dissolving the precipitate produced by the fixed alkali in acetic acid, and adding to this acid solution ferrocyanide of potassium (*see* 186). On *boiling* the filtrate from the iron precipitate, or the solution which has failed to give a precipitate, SESQUIOXIDE OF CHROMIUM is thrown down (M. 3.); this test for chromium must not be relied upon, and therefore the remaining part of the precipitate produced by the general reagent must be examined for chromium in the way described in the next paragraph. To the filtrate from the chromium precipitate, or to the solution which has failed to give a precipitate, add *hydrochloric acid* until the solution is acid; then add *one grain* of *chlorate of potash*, and warm the solution so as to destroy all organic matter (note 2, page 63); add, lastly, *ammonia* in excess. ALUMINA, if present, will be thrown down (L. 2. & 3.) as a white flocculent precipitate, on gently warming the solution; when a precipitate is produced, it must be examined for alumina by the blowpipe test. When iron is present, the original solution must be examined to ascertain in what state of oxidation it exists; for this purpose a portion of the original solution must be examined for PROTOXIDE by means of *ferricyanide of potassium* (183); another portion must be examined for the SESQUIOXIDE by means of the *ferrocyanide of potassium* (186).

173. 3rd. Mix the rest of the washed precipitate with one part of carbonate of soda and three parts of nitrate of potash; fuse the mixture in a porcelain crucible; after the fusion, allow the mass to cool, and then boil it with water, and filter. If the filtrate has a *yellow colour*, SESQUIOXIDE OF CHROMIUM is present; confirm its presence by acidifying the filtrate with *acetic acid*, and then adding a solution of *acetate of lead* (178).

TABLE IV.

Behaviour of the Fourth Group with the Special Reagents.

Alumina ($Al_2 O_3$).	Oxide of Chromium ($Cr_2 O_3$).	Sesquioxide of Iron ($Fe_2 O_3$).	Protoxide of Iron ($F O$).
L. 1. This oxide and its hydrate ($Al_2 O_3$, 3 H O) are *white*.	M. 1. This oxide is green, and its hydrate ($Cr_2 O_3$, 3 H O) a *bluish green powder*.	N. I. This oxide and its hydrate are of a *reddish brown* colour.	O. I. This oxide is *black*, and its hydrate is *white*.
L. 2. *Ammonia, even* in the presence of its salts, precipitates Alumina in the form of Hydrate, which an excess of the reagent *does not* redissolve.	M. 2. *Ammonia, even* in the presence of its salts, precipitates this oxide in the state of Hydrate, which an excess of the reagent *does not* redissolve.	N. 2. *Ammonia, even* in the presence of its salts, precipitates this oxide from its solutions in the form of Hydrate ($Fe_2 O_3$, H O), which an excess of the reagent *does not* redissolve.	O. 2. *Ammonia, but not* in the presence of its salts, precipitates the Hydrated Protoxide (Fe O, H O) from solutions of the protosalts of iron, which an excess of the reagent *does not* redissolve.
L. 3. *The fixed Alkalies* throw down Alumina from its solutions in the form of Hydrate, which *is soluble* in an excess of reagent, from which solution it may be again precipitated on the addition of *Chloride of Ammonium.*	M. 3. The *fixed Alkalies* throw down from solutions of this oxide the Hydrate, which is *soluble* in an excess of the reagent in the *cold;* but on *boiling* the solution, it is again precipitated.	N. 3. *The fixed Alkalies* precipitate from solutions of this oxide the Hydrate, *insoluble* in an excess of the reagent.	O. 3. The *fixed Alkalies* precipitate from solutions of this oxide the Hydrate, *insoluble* in an excess of the reagent.
L. 4. *Carbonate of Ammonia* precipitates from solutions of Alumina the Hydrate. This precipitation is attended with an evolution of carbonic acid.	M. 4. *Carbonate of Ammonia* precipitates from solutions of this oxide the Hydrate, carbonic acid being given off.	N. 4. *Carbonate of Ammonia* precipitates from solutions of this oxide the Hydrate, carbonic acid being given off.	O. 4. *Carbonate of Ammonia* precipitates from solutions of this oxide the Protocarbonate (FeO, CO_2), soluble in chloride of ammonium.

The fixed alkaline carbonates throw down from their solutions all the members of this group, some as oxides, the rest as carbonates. An excess of the reagent does not redissolve the precipitate.

The alkalies fail to precipitate the members of this group in the presence of non-volatile organic matter, such as starch, sugar, tartaric acid, &c.

174. *The following precautions are to be attended to in the analysis of this group:*—Before dissolving the precipitate produced by ammonia, it must be completely freed, by washing it with distilled water, from all trace of ammonia. Dissolve the precipitate in as little acid as possible; for this purpose, pour the acid, small quantities at a time, in a boiling state, upon the precipitate collected upon the filter. If the precipitate be very large, remove it from the filter into an evaporating dish, before adding the acid. The precipitate produced by the soda solution in the cold, must be examined for iron, as it might be due to manganese, which was precipitated by ammonia, and which, like iron, is insoluble in the fixed alkalies.

<center>SPECIAL REMARKS.</center>

175. ALUMINA.—This substance is very abundant in nature. It forms not only the basis of common clay, but is likewise a principal ingredient in many of the precious stones. Along with slight traces of silica and peroxide of iron, it forms the CORUNDUM, SAPPHIRE, RUBY, DIAMANT SPAR, &c. As hydrate, it is known under the names of DIASPORE and GIBBSITE. Combined with silica and glucina, it forms the EMERALD, BERYL, EUCLASE, and CHRYSOBERYL. When pure, it is white; but it frequently possesses a yellowish tint when obtained by drying the hydrate. Its salts are colourless; the soluble ones redden litmus paper, and lose their acids upon ignition. "The insoluble salts are dissolved by hydrochloric acid, with the exception of certain native compounds of alumina; the compounds of alumina which are insoluble in hydrochloric acid are decomposed by ignition with carbonate of soda or bisulphate of potash."—*Fresenius.* The SULPHIDE OF ALUMINUM cannot exist in contact with water, being decomposed into alumina and hydrosulphuric acid.

176. If alumina or any of its compounds be ignited upon

charcoal by the blowpipe flame, afterwards moistened with a few drops of *protonitrate of cobalt*, and again strongly heated, the mass assumes a BLUE COLOUR on cooling. This can only be used as a confirmatory test, as other substances, phosphates and readily fusible salts, exhibit the same reaction.

177. OXIDE OR SESQUIOXIDE OF CHROMIUM.—The colour of this oxide is green; its hydrate is bluish grey. The salts of this oxide have a green or a violet colour; their solutions possess a beautiful green colour by reflected, and reddish violet by transmitted light. The salts of this oxide, which are soluble in water, redden litmus paper. Sulphide of chromium is decomposed in contact with water into oxide of chromium and hydrosulphuric acid. The principal mineral from which this oxide is extracted is the CHROME IRON (FeO, Cr_2O_3), which is found principally in Sweden, in the Uralian Mountains, and in America.

178. When oxide of chromium, or any of its compounds, are fused with nitrate of potash, it becomes converted into a higher oxide, viz., CHROMIC ACID, which, combining with the potash, forms yellow chromate of potash. This potash salt must be dissolved in water and tested for chromic acid by adding acetic acid in excess, and then acetate of lead, when yellow chromate of lead will precipitate. This test distinguishes it at once from all other substances.

179. *Borax* dissolves oxides of chromium and its salts, both in the inner and outer blowpipe flame; the bead, on cooling, assumes an EMERALD-GREEN COLOUR. *Microcosmic salt* has the same effect.

180. In the fixed alkalies, a small quantity of oxide of chromium in the presence of a large quantity of peroxide of iron is totally insoluble; but a small quantity of the latter dissolves readily when a large quantity of the former is present. Under these circumstances, the two oxides are best separated from each other by fusing the mixed substances with *nitre* and *carbonate of*

soda, and treating the fused mass with water; the CHROMATE OF POTASH dissolves in the liquid, whilst the PEROXIDE OF IRON remains behind.

181. PROTOXIDE OR OXIDE OF IRON.—The colour of this oxide is black; its hydrate is white, which, in the moist state, absorbs oxygen from the air very rapidly, acquiring a greyish green, and finally a brownish red, colour. The salts of this oxide are white in their anhydrous, and green in their hydrated, state; their solutions appear coloured only when very concentrated. They turn blue litmus paper red, and are decomposed at a red heat. When dissolved, they absorb oxygen from the air, the oxide being thereby converted into peroxide, which, in a neutral solution, is deposited as a yellow basic salt. Oxidizing agents, such as chlorine and nitric acid, effect this conversion more speedily.

182. *Ferrocyanide of potassium* ($Cy_3 Fe$, $2 K = Cfy$, $2 K$) produces, in solutions of protoxide of iron, a white precipitate of FERROCYANIDE OF IRON AND POTASSIUM ($2 Cfy$, K, $3 Fe$), which speedily becomes *blue* by absorbing oxygen from the air. Free alkalies prevent the formation of this precipitate. It is insoluble in the dilute acids.

183. *Ferricyanide of potassium* ($2 Cfy$, $3 K$) produces a beautiful blue-coloured precipitate of FERRICYANIDE OF IRON ($2 Cfy$, $3 Fe$), which is insoluble in hydrochloric acid, but is decomposed with precipitation of oxide of iron by the alkalies. In highly dilute solutions of protoxide of iron, ferricyanide of potassium produces only a bluish green colouration. If the solution is alkaline, it must be acidified with acetic acid; if it is acid, and the acidity is caused by one of the mineral acids, an alkaline acetate must be added, in sufficient quantity so that the base of the acetate may neutralize the free mineral acid (*see* 188).

184. PEROXIDE or SESQUIOXIDE OF IRON.—This oxide, which

is abundantly spread through nature, has received from mineralogists the name of ILEMATITE. It is of a brownish red colour, and is well known as rust of iron. Its salts usually possess a reddish yellow colour. The soluble neutral salts of mineral acids redden litmus paper, and are decomposed by heat.

185. Soluble SULPHOCYANIDES give to neutral and acid solutions of persalts of iron an intense blood-red colour.

186. *Ferrocyanide of potassium* throws down, even from highly dilute solutions, a beautiful blue precipitate of FERROCYANIDE OF IRON (Prussian blue, Cfy_3, Fe_4), which is insoluble in acids, but is decomposed by the alkalies. In highly dilute solutions of this oxide of iron, only a blue tinge is produced at first; after long standing a scanty precipitate is formed. The same precautions are required in this case as in testing for protoxide with the ferricyanide.

187. *Ferricyanide of potassium* deepens the colour of the solution of persalts of iron to a ruddy brown, but causes no precipitate; if the ferricyanide contains a trace of ferrocyanide,* it will impart to the iron solution a greenish tinge.

188. The ferro- and ferri- cyanide of potassium are decomposed by the mineral acids, green-coloured solutions being formed. In testing, therefore, for iron in acid solutions, it is necessary to avoid this error by the previous addition of an alkaline acetate.

189. Sulphocyanide of potassium (K, Cy S_2) produces in neutral, and even in moderately acid, solutions of sesquioxide of iron a very intense blood-red colour, arising from the formation of a soluble SULPHOCYANIDE OF IRON; it disappears on the addition of alkalies, or of a large quantity of strong acid. This is by far the most delicate test for sesquioxide of iron.

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* The solution of ferricyanide of potassium ought to be made as it is wanted, as the ferricyanide decomposes when in a state of solution, a trace of ferrocyanide being formed.

The following SALTS, *being insoluble in Neutral and Alkaline Solutions, are precipitated along with the members of the Fourth Group.**

PHOSPHATE OF ALUMINA; THE PHOSPHATES OF IRON AND THE PHOS-PHATES AND OXALATES OF THE ALKALINE EARTHS, WITH THE EXCEPTION OF OXALATE OF MAGNESIA.

190. PHOSPHATE OF ALUMINA behaves in the same way with reagents as pure alumina, with this exception, that it is insoluble in *acetic acid* whilst pure alumina is soluble. The presence of phosphoric acid, when combined with alumina, may be detected by the following method:—After having *dissolved* the alumina compound in a small quantity of hydrochloric acid, *tartaric acid* must be added, and then *ammonia* in *excess*. If on the addition of *sulphate of magnesia* to this solution a precipitate be formed, PHOSPHORIC ACID is present. When the quantity of acid present is small, the precipitate will not appear until after the lapse of some time; in all cases the formation of the precipitate is much promoted by agitation (*consult* par. 389).

191. The phosphoric acid in phosphate of alumina may also be detected in the following way:—" Add carbonate of soda to the hydrochloric acid solution until the free acid is nearly neutralized; mix with carbonate of baryta in excess, add solution of soda or potash, and boil. This process gives the alumina in solution, the phosphoric acid in a precipitate of phosphate of baryta. Dissolve this precipitate in hydrochloric acid, decompose by sulphuric acid, filter, and test the filtrate with sulphate of magnesia, with addition of chloride of ammonium and ammonia."
—*Fresenius.*

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* The student will do well to omit this section of the group until he has had some practice in detecting the more simple combinations of acid and base.

192. Phosphoric acid may be detected in almost all salts and most minerals containing it, in the following way:—" If some molybdate of ammonia is mixed in a test-tube with hydrochloric acid or nitric acid in sufficient quantity to redissolve the precipitate which forms at first, and a little of a very dilute fluid containing phosphoric acid is then added, and the mixture boiled, the fluid acquires an intensely yellow colour, and after some time a yellow precipitate separates, which is insoluble in hydrochloric acid. As the yellow compound is decomposed by free phosphoric acid, an excess of the fluid containing the phosphoric acid must be carefully avoided. The yellow precipitate may, when it has subsided, be perceived even in dark-coloured fluids."
—*Fresenius.*

193. PHOSPHATE OF IRON behaves in the same way with reagents as the peroxide, with this exception, that it is insoluble in *acetic acid*, in which reagent the latter is soluble. *Sulphide of ammonium* decomposes PHOSPHATE OF IRON, precipitating the metal in the state of sulphide whilst the acid remains in solution in combination with the ammonia. The phosphoric acid is therefore sought for in the filtrate and not in the precipitate, when sulphide of ammonium has been employed as the precipitating reagent. The same method may be employed for the detection of phosphoric acid when combined with iron, as is employed when this acid is in combination with alumina.

194. PHOSPHATE OF LIME (bone earth 3 CaO, PO$_5$) is soluble in *acetic acid*. This salt may be decomposed in several ways. The following are those which are most applicable in qualitative analysis:—1. Dissolve the phosphate in a small quantity of hydrochloric acid; add to the solution *acetate of potash*, and after that a few drops of *perchloride of iron* (consult par. 385). PHOSPHATE OF IRON will be precipitated, whilst the LIME will remain in solution

along with the excess of the perchloride of iron employed.   To
detect the LIME, throw down the iron by sulphide of ammonium,
and add to the filtrate *oxalic acid*.   If a precipitate be produced,
lime is present.   2. Dissolve the phosphate in a small quantity of
nitric acid; add to this solution *protonitrate of mercury,* and then
ammonia slightly in excess; PHOSPHATE OF MERCURY along with
the excess of OXIDE OF MERCURY will be precipitated, whilst the
LIME will remain in solution, from which solution it will be
thrown down on the addition of *oxalic acid.*   Boil the mixed
precipitate of phosphate of mercury and oxide of mercury in
sulphide of ammonium; filter, and to the filtrate add *chloride of
ammonium* and *sulphate of magnesia :* if a precipitate be pro-
duced, it proves the presence of phosphoric acid.   The above
remarks upon PHOSPHATE OF LIME will apply to the corresponding
salt of BARYTA, STRONTIA, and MAGNESIA.

195. OXALATE OF LIME is insoluble in *acetic acid.*   By ignition,
this salt, like all the other oxalates, is decomposed, a carbonate
being left.   To separate the oxalic acid from the lime, add to a
nitric solution of this salt *protonitrate of mercury.*   OXALATE OF
MERCURY will be precipitated, whilst the lime, in the state of nitrate,
will remain in solution along with the excess of protonitrate of
mercury employed.   To detect the LIME, precipitate the mercury
by ammonia, and add to the filtrate *oxalic acid.*   OXALATE OF
MERCURY is decomposed by boiling it in *sulphide of ammonium,*
the metal being precipitated as sulphide, whilst the acid remains
in combination with ammonia, in which solution it may be
detected on the addition of any soluble *lime salt.*   The above
remarks will apply to the corresponding SALT OF BARYTA and
STRONTIA.

TABLE V.:—PRECIPITATE PRODUCED BY AMMONIA IN THE HYDROSULPHURIC ACID FILTRATE.

Dissolve in boiling dilute Nitric Acid.—Add an excess of Caustic Soda in the cold.

FILTRATE

Sesquioxide of Chromium; Alumina, Phosphate of Alumina. Boil for some time.

- **PRECIPITATE** Sesquioxide of Chromium.
- **FILTRATE**; Alumina; Phosphate of Alumina. Add Acetic Acid in excess.
  - **PRECIPITATE** Phosphate of Alumina.
  - **FILTRATE** Alumina; add Phosphate of Soda.
    - **PRECIPITATE** Phosphate of Alumina.

PRECIPITATE

Peroxide of Iron, Perphosphate of Iron, and when in combination with Oxalic or Phosphoric Acids, Baryta, Strontia, Lime; also Magnesia, when in combination with Phosphoric Acid.

Dissolve in boiling dilute Nitric Acid, then add Tartaric Acid, and finally Ammonia in excess.

FILTRATE

Pernitrate of Iron; Perphosphate of Iron. Divide the solution into two parts.

- To one part add Acetic Acid, until the solution possesses an acid reaction; then add Ferrocyanide of Potassium.

  If a blue precipitate is formed, it shows the presence of Iron.

- If iron has been found, add to the other part Chloride of Ammonium and Sulphate of Magnesia.

  If a precipitate is formed after agitating the fluid and allowing it to stand for some time, it shows the presence of Phosphoric Acid.

NOTE.—To ascertain whether there was any Iron, uncombined with Phosphoric Acid, add to the original solution Acetate of Soda; filter, and to the filtrate add Ferrocyanide of Potassium.

If a blue precipitate is formed, it proves that all the iron did not exist as phosphate.

PRECIPITATE

The Phosphates and Oxalates of the Alkaline Earths.

Dissolve in Nitric Acid, and add protonitrate of Mercury.

- **PRECIPITATE** Oxalate of Mercury.

  Confirm the presence of Oxalic Acid, by boiling the Mercury precipitate in Sulphide of Ammonium; filter, acidify with acetic acid; filter if necessary, and then add to the solution Sulphate of Lime.

  If a precipitate is formed, Oxalic Acid is present.

- **FILTRATE** Baryta, Strontia, or Lime, originally in combination with Oxalic Acid and the Phosphates of the Alkaline Earths, along with the excess of Protonitrate of Mercury. Add Ammonia slightly in excess.

  - *Precipitate* Phosphate of Mercury along with the excess of Oxide of Mercury. Boil the precipitate in Sulphide of Ammonium; filter, and to the filtrate add Chloride of Ammonium and Sulphate of Magnesia.

    If a Precipitate is formed after agitating the liquid and allowing it to stand for some time, it proves the presence of Phosphoric Acid.

  - *Filtrate* Baryta, Strontia, Lime, and Magnesia. Examine the filtrate for the Alkaline Earths, according to the method already given.

196. *The following precautions are to be attended to in the analysis of this section:*—Before dissolving the precipitate produced by ammonia, it must be completely freed by washing from all trace of that reagent. Frequently a small precipitate will appear after boiling the caustic soda solution, when oxide of chromium is absent; the presence of this member must therefore in all cases be confirmed by other tests. Alumina and phosphate of alumina are sometimes overlooked by the operator, from his neglecting to add acetic acid in excess. The precipitate produced by caustic soda, after being well washed, should be dissolved in as small a quantity of nitric acid as possible, to which solution a moderate quantity of tartaric acid should be afterwards added, and finally ammonia in excess; the solution ought, after the addition of these reagents, to be well agitated, and time allowed for the separation of the precipitate. In testing for phosphoric acid in the ammoniacal solution, a precipitate will frequently be formed on the addition of sulphate of magnesia when phosphoric acid is absent. To distinguish the phosphate precipitate from this, the precipitate produced ought to be dissolved in tartaric acid, and ammonia added in excess. If a precipitate again appears, after agitating the liquid and allowing it to stand, it must be due to the presence of phosphoric acid. The precipitate produced by ammonia in the tartaric acid solution must be well washed before dissolving it in dilute nitric acid. A slight turbidness will generally be formed on the addition of nitrate of mercury to the nitric acid solution, even in the absence of oxalic acid, owing to the nitric acid containing a slight trace of chlorine.

197. When substances are examined, the nature of which is a sufficient proof that the phosphate and oxalate of baryta and strontia must be absent, as in the case of *natural and artificial manures, soils,* etc., a simpler method may be employed for separating OXALATE OF LIME, PHOSPHATE OF LIME, and PHOS-PHATE OF MAGNESIA, from each other, than the one given in

the table. After separating them from all the other substances, dissolve the precipitate, produced by ammonia in the tartaric acid solution, in a small quantity of hydrochloric acid, and to this solution add *acetate of soda* in excess. OXALATE OF LIME, if present, will be precipitated, whilst the phosphates of lime and magnesia will remain in solution. Filter, and to the filtrate add *oxalic acid*, which will precipitate the LIME existing originally as PHOSPHATE, in the state of OXALATE. PHOSPHATE OF MAGNESIA will be precipitated from this filtrate on the addition of *ammonia* in excess.

APPENDIX TO THE FOURTH GROUP.

198. SESQUIOXIDE OF URANIUM ($U_2 O_3$).—This oxide is of a brick-red colour, its hydrate is yellow; by ignition it loses part of its oxygen, being converted into $U_3 O_4$, the colour of which is a very dark green, approaching black. The sesquioxide dissolves in acids, forming salts, the solutions of which have a fine yellow colour, and redden blue litmus paper. Hydrosulphuric acid reduces this oxide to the state of protoxide; the last-named oxide attracts oxygen from the air, becoming converted into the sesquioxide again: oxidizing agents have the same effect as the oxygen of the air.

199. Sulphide of ammonium precipitates, from alkaline solutions of this oxide, black sulphide of uranium, which subsides slowly, and is readily soluble in acids, even in acetic acid.

200. The volatile and fixed alkalies precipitate this oxide from its solutions completely, in the form of a yellow precipitate, which is insoluble in an excess of the reagent.

201. Carbonate of ammonia produces a yellow precipitate, which is soluble in an excess of the reagent, but is deposited again from this solution on boiling. It differs from sesquioxide of iron in its behaviour with this reagent, which it so closely resembles in its behaviour with the other reagents.

202. Ferrocyanide of potassium produces in solutions of this oxide a fine brown-red precipitate; this is a very delicate test for uranium.

FIFTH GROUP.

PROTOXIDE OF TIN.   PEROXIDE OF TIN.   OXIDE OF ANTIMONY.
ARSENIOUS ACID.   ARSENIC ACID.   PEROXIDE OF GOLD.   PER-
OXIDE OF PLATINUM.

203. All the members of this group possess, in a greater or less
degree, the character of acids. Arsenious and arsenic acids are
soluble in water; the rest are insoluble, not only in water, but
likewise in nitric acid. They are all readily soluble in concen-
trated hydrochloric acid. In the state-of sulphides they behave
with different reagents in the following manner:—the protosulphide
and bisulphide of tin, with the sulphide of antimony, are insoluble
in nitric acid, but dissolve readily in concentrated hydrochloric
acid; whereas sulpharsenious and sulpharsenic acids are insoluble
in hydrochloric acid, but are easily soluble in concentrated nitric
acid. These different sulphides are readily dissolved by the
alkalies and alkaline sulphides, from which solutions they are
again precipitated unaltered on the addition of any acid in excess.
The sulphides of gold and platinum are insoluble both in hydro-
chloric and nitric acid, but are easily soluble in aqua regia (a
mixture of the two acids). The sulphides of arsenic and bisul-
phide of tin are *yellow;* sulphide of antimony is *orange;* proto-
sulphide of tin is *dark brown;* and the sulphides of gold and
platinum are *black.* They also dissolve with difficulty in the
alkalies and alkaline sulphides.

204. As gold and platinum are seldom met with in ordinary
analysis, and as many of their properties render them perfectly
distinct from the rest of the members, it has been found of advan-
tage to subdivide the group. The first division comprises the
OXIDES of TIN, ANTIMONY, and ARSENIC; the second, the OXIDES of
GOLD and PLATINUM.

FIRST DIVISION.

205. The precipitate produced by the general reagent, after

having been well washed, must be treated with a dilute solution of *carbonate of ammonia*.* Both SULPHIDES of ARSENIC, being soluble in that reagent, will pass into solution; whilst the SULPHIDES of ANTIMONY and TIN, being insoluble, will remain undissolved. The solution must be separated from the insoluble sulphides by filtration. If a *yellow precipitate* be produced on the addition of *hydrochloric acid* to the filtrate, one or both SULPHIDES of ARSENIC must be present. The substance which was insoluble in carbonate of ammonia, after having been well dried, must be mixed with three parts of *nitrate of ammonia*,† and the mixture projected in small portions into a porcelain crucible containing two parts of nitrate of ammonia in a state of liquefaction. After all fuming has ceased, the residue should be gently ignited for a short time and then allowed to cool. The residue must be subsequently heated with a saturated solution of *tartaric acid*. If complete solution takes place, OXIDE of ANTIMONY only can be present. If a portion remain undissolved by the tartaric acid, it indicates the probable presence of TIN. When complete solution does not take place, the liquid must be filtered, and to the filtrate must be added *hydrochloric acid* and subsequently *hydrosulphuric acid*. If an *orange-red coloured precipitate* be formed, OXIDE of ANTIMONY is present. The substance insoluble in tartaric acid must be examined for tin by fusing it with *carbonate of soda* and *cyanide of potassium*, as directed under the special remarks of the peroxide of that metal.

206. *The following precautions must be attended to in analizing this group:*—The mixed precipitate must be agitated in a test-

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* *See* Appendix A.

† When the amount of precipitate is so small that little or nothing can be detached from the filter, the precipitate as well as the filter, after having been cut into small pieces, must be mixed up with the nitrate of ammonia, and subsequently projected into the crucible.

tube for a few seconds only, with a dilute solution of carbonate ammonia,* and then quickly filtered. When only a slight trace of arsenic is present, the carbonate of ammonia solution, on the addition of hydrochloric acid, will simply assume a slight yellow colour, no distinct precipitate being formed. When arsenic is present, the original solution must be examined to ascertain in what state it exists, whether as arsenious or arsenic acids.

SPECIAL REMARKS.

207. OXIDE OF TIN (Sn O).—This oxide is black, its hydrate being white. Nitric acid and nitrates in a state of fusion convert it into the peroxide. The protosalts of tin are colourless, and are decomposed by heat. The soluble neutral salts redden litmus paper, and are decomposed, in the presence of much water, into soluble acid and insoluble basic salts. The addition of water therefore to the protosalts of tin produces a milkiness which disappears on the addition of hydrochloric acid. Sulphide of tin (SnS) is of a dark brown colour.

208. The *alkalies* and their *carbonates* throw down from solutions of this oxide the HYDRATE (SnO, HO), which is easily soluble in solutions of the fixed alkalies, but insoluble in ammonia and the alkaline carbonates.

209. All protosalts of tin are powerful reducing agents, from the great affinity they have for an additional quantity of oxygen. Many metallic oxides, such as the oxides of gold, silver, and mercury, are reduced to the metallic state in their presence; whilst other oxides, such as peroxide of iron and oxide of copper, are reduced to a lower degree of oxidation.

210. *Perchloride of gold* produces in solutions of protosalts of tin, containing a small quantity of free nitric acid, a beautiful PURPLE PRECIPITATE (purple of cassius).

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* According to Blyth, the dilute solution must be prepared by dissolving one ounce of solid carbonate of ammonia in twelve fluid ounces of water.

211. Solution of perchloride of mercury produces in solutions of protoxide of tin a white precipitate of protochloride of mercury, owing to the protosalt of tin withdrawing half the chlorine from the perchloride of mercury. If sufficient quantity of the tin compound be present, it removes, after a time, all the chlorine from the mercury; the colour of the precipitate then becomes grey. Since this reaction takes place even in highly dilute solutions, and in the presence of much free hydrochloric acid, it is very valuable for the detection of oxide of tin.

212. Peroxide of Tin (SnO_2).—This oxide is of a light straw colour; its hydrate is white. Nitric acid converts metallic tin and its protoxide into the hydrated peroxide, which is deposited in the form of a white powder. A peroxide of tin is likewise precipitated from persalts of tin, on the addition of caustic soda to their solutions. These hydrates, although they have the same composition, are perfectly distinct in their chemical properties. The one formed by the action of nitric acid is insoluble, both in acids and the fixed alkalies; the other is soluble in these reagents. These modifications are capable of being transformed into each other. The insoluble one is rendered soluble by fusion with the carbonated alkalies; the soluble is converted into the insoluble form by ignition. Bisulphide of tin ($Sn S_2$) is of a yellow colour. The usual mineral of this metal is the peroxide (*tin stone* SnO_2).

213. The *alkalies* and their *carbonates* precipitate from solutions of persalts of tin the HYDRATE, which is soluble in the fixed caustic alkalies, but insoluble in ammonia and the alkaline carbonates.

214. If per- or proto- compounds of tin be mixed with equal parts of *carbonate of soda* and *cyanide of potassium*, and the mixed mass be subjected, upon a charcoal support, to the inner blowpipe flame, *ductile metallic grains of* TIN will be obtained, unaccompanied by any incrustation upon the charcoal.

215. Oxide of Antimony ($Sb O_3$).—This oxide occurs either

in the form of white brilliant crystalline needles, or as a greyish white powder, assuming the one or the other of these forms according to its mode of preparation. It fuses at a gentle red heat, and, when exposed to a higher temperature, volatilizes unaltered. The solubility of this oxide in tartaric acid distinguishes it from the other members of the group. When fused along with nitrates, it is converted into a higher oxide (antimonic acid, $Sb\,O_5$).

216. Some of the salts of antimony are decomposed by ignition; some are volatilized unaltered. The soluble neutral salts redden litmus paper. When treated with a large amount of water, they are decomposed into soluble acid and insoluble basic salts. In this respect they resemble the salts of bismuth: with this exception, that the insoluble basic salts of antimony dissolve in tartaric acid, whilst the corresponding salts of bismuth are insoluble. Sulphide of antimony ($Sb\,S_3$) is of an orange-red colour. The principal mineral of this metal is the sulphide.

217. The *alkalies* and their *carbonates* throw down from solutions of antimony a bulky precipitate of OXIDE OF ANTIMONY, which is soluble in the fixed caustic alkalies and the alkaline carbonates, but insoluble in ammonia.

218. "*Metallic zinc* precipitates from all solutions of salts of teroxide of antimony, if they contain no free nitric acid, *metallic antimony* as a black powder. But if the solution contains free nitric acid, teroxide of antimony precipitates together with the metal."

219. If a solution of teroxide of antimony is brought into contact with zinc and dilute sulphuric acid, the zinc oxidizes not only at the expense of the water, but also at the expense of the teroxide of antimony; the antimony is, consequently, reduced to the metallic state: a portion of the antimony, however, at the moment of its reduction, enters into combination with some of the liberated hydrogen, forming with that element a gaseous com-

pound — terhydride of antimony ($Sb\ H_3$). " If this gaseous compound be dried by passing it through a tube, the anterior portion of which is loosely filled with cotton wool, and the remoter part with chloride of calcium, and be then allowed to escape from a tube of *hard glass* drawn out to a fine point, the presence of antimony may be recognized by the following reactions:—·

220. " 1st. The gas will burn with a *bluish green flame*, emitting white fumes of *teroxide of antimony*, which may be condensed in a cold beaker, dissolved in *hydrochloric acid*, and tested with *hydrosulphuric acid*.

221. " 2nd. If the inner surface of a porcelain capsule be depressed upon the flame, a *black spot* of metallic antimony will be deposited upon it, which is lustrous only when in thin layers. This coating of metal may be dissolved in *aqua regia* and tested. (The operator should take care to prove, before commencing this experiment, that the flame of the hydrygen itself deposits no spot upon porcelain.)

222. " 3rd. The glass tube from which the gas issues should be heated with a spirit lamp, in the centre; a *lustrous mirror of antimony* will be deposited on the inside of the tube, immediately around the flame of the lamp, whilst the bluish green tint of the hydrogen flame in great measure disappears.

223. " These reactions should be compared with those of terhydride of arsenic under similar circumstances.

224. " If granulated zinc be boiled with a solution of antimony, to which a very large excess of *potash* has been added, the hydrogen which is evolved is free from terhydride of antimony."

225. If compounds of antimony, mixed with *carbonate of soda* and cyanide of potassium, be exposed, upon a charcoal support, to the reducing flame of the blowpipe, brittle grains of *metallic* antimony will be formed, accompanied with a *white* incrustation on the charcoal.

226. ARSENIOUS ACID (AsO_3).—There are two varieties of this acid, which are perfectly distinct in their physical characters and chemical properties. One, from its appearance, is termed the vitreous, and the other the milky variety; when heated, they volatilize in white inodorous fumes. "If the operation is conducted in a glass tube, a sublimate is obtained, consisting of small brilliant octahedrons and tetrahedrons." Both kinds are more easily soluble in hot than in cold water. This acid is exceedingly poisonous; and, being altogether inodorous, almost destitute of taste, and readily obtainable, is frequently employed as a poison. The best antidote is the moist and well washed hydrated sesquioxide of iron.

227. This acid unites with bases, forming a class of salts called arsenites, which are all insoluble in water, with the exception of the alkaline arsenites. Sulpharsenious acid (AsS_3) is yellow, and soluble, not only in the alkalies and alkaline sulphides, but likewise in the alkaline carbonates.

228. *Nitrate of silver* produces in neutral solutions of the arsenites a yellow precipitate of ARSENITE OF SILVER (2 AgO, AsO_3), soluble in nitric acid and ammonia.

229. *Sulphate of copper* produces in neutral solutions of the arsenites a yellowish green precipitate of ARSENITE OF COPPER (2 CuO, AsO_3).

230. If to a solution of arsenious acid, or an arsenite, *caustic potash* be added in excess, and a few drops only of a dilute solution of *sulphate of copper*, and the liquid subsequently boiled, a red precipitate of *suboxide of copper* (Cu_2O) will fall down, whilst the solution will contain ARSENIATE OF POTASH. This test is particularly applicable in distinguishing arsenious from arsenic acid. It cannot be employed with safety as a direct means for detecting arsenious acid, as many organic substances possess the property of reducing protoxide of copper to the state of suboxide.

231. "If to arsenious acid, no matter whether in the solid form or in solution, some *acetic acid* is added, and then *potash* in slight excess, the mixture evaporated to dryness, and the residue heated to redness in a small tube—or if a trace of arsenious acid is introduced into a narrow test-tube, and then covered with a somewhat larger quantity of acetate of soda, and heat applied—part of the arsenious acid is reduced, but there forms at the same time ALKARSIN (oxide of cacodyl, $C_4 H_6 AsO$), which makes its presence immediately known by its equally characteristic and formidable odour, which somewhat resembles that of sharp onions. This changes speedily to the not less characteristic odour of chloride of cacodyl, if the ignited contents of the tube are heated with a few drops of protochloride of tin."—*Bunsen.*

232. If clean metallic copper is boiled in a solution containing arsenious acid, and acidified with hydrochloric acid, the copper becomes coated with a *steel-grey film* of metallic arsenic; if the quantity of arsenious acid is considerable, the reduced arsenic will separate from the copper, when the liquid is boiled for a considerable time, in *large black scales*. As many other metallic oxides are reduced to their metallic state under the same circumstances, it is necessary to submit the crust to further examination. This test, which is called "Reinsch's test," is particularly useful for the detection of arsenic in organic liquids or solids. "The suspected liquid is simply to be acidulated with about one sixth of its bulk of hydrochloric acid, and boiled. The solid tissue must be cut up into very small pieces, and boiled for some time in a mixture of about one part of hydrochloric acid with six of water, until the whole is completely disintegrated; then strained through muslin, or filtered through a previously wetted filtering paper.

233. "Into either of the above boiling liquids, dip the end of a piece of clean polished wire; examine the wire from time to time, and as soon as its surface acquires a grey metallic discolouration, remove it, and add in its stead fragments of fine

copper gauze, continuing the supply as long as the last added piece assumes any definite alteration in colour.

234. "Remove the pieces of copper gauze, wash them in water, and dry them between folds of filtering paper; the deposit will not rub off unless the amount of arsenic be very large. If the arsenic exists in but very small quantity, the colour of the precipitated metal is bluish; otherwise, of a dark iron-grey tint. Holding the piece of gauze in the fingers, warm it over a flame, coil it up into a small compass, and introduce it into a reduction-tube; now apply heat cautiously; the arsenic will volatilize, oxidize, and condense in the cold part, in the form of a white crystalline sublimate. Several pieces of coated gauze may be thus treated successively, until a sufficiently obvious sublimate of arsenious acid is procured; by examination with a lens, or with the low power of a microscope, the crystals will be seen to consist of highly iridescent octo- and tetra- hedra."— *Odling's Practical Chemistry.*

235. File off the piece of tube containing the sublimate, boil it for a minute or two in a little water; test the water, after the boiling, for arsenious acid, one portion with hydrochloric and hydrosulphuric acids, and another portion with nitrate of silver.

236. Arsenic, as well as antimony (219), combines with hydrogen in its *nascent* state, forming an inflammable gaseous compound, which burns with a bluish white flame, water and arsenious acid being formed; water and teroxide of antimony being formed when terhydride of antimony is burned. When free access of air is prevented, the hydrogen only is oxidized, metallic arsenic (or if it is terhydride of antimony, metallic antimony) being deposited in a finely divided state.

237. If, therefore, a solution of arsenious acid or an arsenite be brought into contact with zinc and dilute sulphuric acid, the zinc oxidizes not only at the expense of the water, but also at the expense of the arsenious acid; and the arsenic, at the moment of

its reduction, enters into combination with the hydrogen, forming with that element the gaseous compound, terhydride of arsenic ($As\ H_3$): this gaseous compound was discovered by the late Mr. Marsh, and applied by him in the detection of arsenic. If the reduction of the arsenious acid, and the conversion of the arsenic into terhydride of arsenic, be conducted in a flask fitted with an evolution-tube, the gas compound can then be subjected to the following experiments:—The evolution-tube must consist of a drying-tube, into one end of which is fitted a narrow tube of *hard glass*. The drying-tube is placed nearest the flask, and it is half filled with cotton wool, and half with fragments of chloride of calcium; the end nearest the flask is filled with the wool. The hard glass tube should be from six to nine inches long, and drawn out at one end, so as to form a jet, where the gas may be burned. The gas may be examined in the following manner:—

238. 1st. " Terhydride of arsenic burns with a *livid blue flame*, producing *arsenious acid*, which may be condensed in a cold beaker, dissolved in *hot water*, and tested (especially with *nitrate of silver*, and with *hydrochloric* and *hydrosulphuric acids*).

239. 2nd. " By depressing the inner surface of a porcelain capsule * upon the flame, a *black* (generally) *lustrous spot of metallic arsenic* is obtained (this experiment should always be tried with the hydrogen flame, † before the arsenical solution is poured into the evolution-bottle); this spot may be tested by dissolving in *concentrated nitric acid*, evaporating just to dryness upon a sand bath, adding *water* and afterwards *nitrate of silver*, with, if necessary, a little *dilute ammonia*, when a brick-red

* " The porcelain should not be allowed to remain in the flame for more than a second or two, since the minute spots would be dispelled if the porcelain were to become very hot."

† " A great obstacle to the employment of Marsh's test is the difficulty of obtaining zinc and sulphuric acid perfectly free from arsenic, for which they should be very carefully tested previously to use."

precipitate of *arseniate of silver* will be obtained; an antimony spot, when treated in this way, generally gives a slight dirty-white precipitate with nitrate of silver.

240. " The incrustation of arsenic (whether on a porcelain surface or in a glass tube) may be dissolved by solution of *chloride of lime*, which does not affect the antimony incrustation: this test may serve, to some extent, to distinguish the two metals, but is not adequate to the detection of traces of antimony in a mirror of arsenic."—*Abel and Bloxam*.

241. The properties and reactions just described enable us to distinguish pure arsenical stains and mirrors from antimonial stains and mirrors, but they do not enable us to detect arsenic with positive certainty in the presence of antimony. To obtain positive evidence, the following method ought to be employed:— The central part of the glass tube (which ought to be free from lead) through which the gas passes should be heated to redness; this effects the decomposition of the gaseous compound, the metal being deposited in a finely divided state. A feeble stream of dry hydrosulphuric acid gas must now be transmitted through the tube, the metallic mirror being heated from its outward to its inward extremity. If only arsenic be present, the yellow sulphide of that metal will be formed. If antimony only be present, the orange or black sulphide of antimony will be produced; but if both metals be present, the corresponding sulphides will be formed; and the sulphide of arsenic, being the more volatile of the two, will be the further removed from the flame. A stream of dry hydrochloric acid gas must be passed through the tube without the application of heat: by this means the sulphide of antimony will be converted into the volatile chloride, which will entirely disappear; whilst the sulphide of arsenic will remain unaltered, and may be distinguished from any sulphur which may have separated, by dissolving readily in ammonia.

242. " If arsenites, or arsenious acid, or tersulphide of arsenic,

are fused together with a mixture of equal parts of dry *carbonate of soda* and *cyanide of potassium*, the whole of the arsenic is reduced to the metallic state, and, if an easily reducible base, the latter also; the eliminated oxygen converts part of the cyanide of potassium into cyanate of potash (KO, CyO). In the reduction of tersulphide of arsenic, sulphocyanide of potassium (K, Cy S$_2$) is found. The operation is conducted as follows:—Introduce the perfectly dry arsenical compound into the bulb of a small bulb-tube, and cover it with six times the quantity of a perfectly dry mixture of carbonate of soda and cyanide of potassium. The whole quantity must not more than half-fill the bulb, otherwise the fusing cyanide of potassium is likely to ascend into the tube. Apply the heat of a spirit lamp to the bulb, and continue this for a while, as the arsenic frequently requires some time for its complete sublimation. The metallic mirrors are deposited on the cold part of the tube; they are of exceeding purity. They are obtained from all arsenites whose bases remain either altogether untouched, or are reduced to such metallic arsenides as lose their arsenic partly or totally upon the simple application of heat. This method deserves to be particularly recommended on account of its simplicity and neatness, as well as for the accuracy of the results attainable by its application, even in cases where only very minute quantities of arsenic are present. It is more especially adapted for the direct production of arsenic from tersulphide of arsenic, and is in this respect superior to all other methods hitherto suggested. The delicacy of the reaction may be very much heightened by heating the mixture in a stream of dry carbonic acid gas. A series of experiments made by *Dr. V. Babo* and myself has shown that the most accurate and satisfactory results are obtained in the following manner" (Fresenius):—

243. The apparatus consists of a flask or two-necked bottle capable of holding about eight or twelve fluid ounces; this flask

or bottle is fitted with a funnel-tube, and a bent tube which dips into another and smaller flask.   In the first flask carbonic acid is slowly generated from pretty large fragments of marble (no powder) and dilute hydrochloric acid; it is conveyed by the conducting-tube into the smaller flask, which is partly filled with concentrated sulphuric acid, in order to dry the gas.   The conducting-tube from the small flask is bent at right angles, and connected, by means of a cork, with the reduction-tube; this latter tube is made ont of a piece of hard glass tube (combustion-tube) somewhat more than $\frac{3}{8}$ inch in diameter, and drawn out at one extremity to a long point; the length of the body of the tube should be about 4 inches, that of the point at least $2\frac{1}{2}$ inches.

244. A mixture of three parts of dry *carbonate of soda* and one part of cyanide of potassium is dried in the water bath; one part of arsenical sulphide, or the arsenite, which has been also dried in the water bath, is mixed with about twelve parts of the well dried mixture of carbonate of soda and cyanide of potassium. The mixture, before it has time to get damp, is put npon a narrow slip of card-paper bent into the shape of a gutter; it is then introduced into the tube, and the latter is turned half round upon its axis; the mixture falls npon the glass, and the gutter mnst be withdrawn.   The mixture should be in the middle of the tube, and it ought not to occupy more than an inch.   The reduction-tube must now be fixed, by means of the cork, to the conducting-tube of the small flask, and a moderate stream of carbonic acid onght to be evolved, by pouring some hydrochloric acid into the large flask, by means of the funnel-tube.   Heat the reduction-tube, in its whole length, very gently with a spirit lamp, until the mixture is perfectly dry; when all the water is expelled, moderate the gas stream so that only one bubble shall pass through the sulphuric acid in the small bottle *in a second;* the gas stream may be moderated by pouring water into the large flask by means of the funnel-tube.   When the gas stream is moderated, apply

the flame of a spirit lamp to the shoulder of the tube; and when this part of the tube is red hot, apply the flame of a second and larger spirit lamp, commencing at the end of the reduction-tube nearest the conducting-tube of the small flask, and heating along up to the mixture; continue to apply the flame at the part where the mixture is until all the arsenic is expelled. The far greater portion of the volatilized arsenic recondenses in the narrow part of the tube, whilst an extremely minute portion only escapes through the fine point, imparting to the surrounding air the peculiar odour of garlic. Advance the flame of the second spirit lamp slowly and gradually up to the first, by which means the whole of the arsenic which may have condensed in the wide part of the tube is driven into the narrow part. When this end has been attained, close the fine point of the tube by fusion, and apply heat, proceeding from the closed point towards the part where the greater part of it is condensed; by which means the extent of the mirror is narrowed, whilst its beauty and lustre are correspondingly increased. In this manner, perfectly distinct mirrors of arsenic may be produced from as little as the $\frac{1}{300}$th part of a grain of tersulphide of arsenic. No mirrors are obtained by this process from tersulphide of antimony, nor from any other compound of antimony.

245. If a solution containing arsenious acid, or an arsenite, be mixed with a large excess of a concentrated solution of caustic potash, and boiled with fragments of granulated zinc, terhydride of arsenic is evolved, and may be readily recognized by allowing it to pass on to a piece of filter-paper moistened with a solution of nitrate of silver; the paper assumes a purplish black colour, even when a small quantity of arsenic is present. This test serves to distinguish arsenic from antimony.—*Fleitmann.*

246. Arsenious acid, when mixed with a little carbonate of soda, and subjected to the inner blowpipe flame on charcoal, evolves a peculiar garlic odour, supposed to arise from a lower

oxide. The vapours of arsenious acid, when sublimed from a piece of glass, possess no odour.

247. ARSENIC ACID (AsO_5). — This oxide is white; it is deliquescent and strongly acid, forming, with bases, a class of salts called arseniates, which are all insoluble in water, with the exception of the alkaline arseniates. It fuses at a low red heat without undergoing decomposition, but at a higher temperature is resolved into oxygen and arsenious acid, which volatilize. Sulphurous acid, aided by a gentle heat, reduces it likewise to this lower state of oxidation. The metal arsenic is found in nature principally as sulphide.

248. *Nitrate of silver* produces, in neutral solutions of the arseniates, a reddish brown precipitate of ARSENIATE OF SILVER ($3\ Ag\ O, As\ O_5$), soluble in dilute nitric acid and in ammonia.

249. *Sulphate of copper* produces, in neutral solutions of the arseniates, a greenish blue precipitate of ARSENIATE OF COPPER ($2\ Cu\ O, HO, AsO_5$).

250. *Sulphate of magnesia*, in the presence of chloride of ammonium and ammonia, produces, in solutions of the arseniates, a white precipitate of ARSENIATE OF AMMONIA AND MAGNESIA ($2\ MgO, NH_4O, AsO_5$), soluble in acids.

251. In those reactions which depend upon the reduction of the arsenic to the metallic state, arsenic resembles arsenious acid.

SECOND DIVISION.

252. Gold and platinum produce reactions so decisive—the former with chloride of tin, and the latter with chloride of ammonium—that their presence may invariably be detected in the presence of all the other metals. The original solution may therefore in all cases be examined for these substances.

253. PEROXIDE OF GOLD ($Au\ O_3$).—This oxide is of a deep brown colour, its hydrate being somewhat lighter in colour. They

both dissolve readily in hydrochloric acid, but are insoluble in dilute oxygen acids. Persulphide of gold ($Au S_3$) is black.

254. The salts of the protoxide of iron precipitate gold as a *bluish black* precipitate, which acquires a metallic lustre when rubbed.

255. A solution of protochloride of tin and some bichloride produce, even in very dilute solutions of gold, a purple precipitate (purple of Cassius), "the tint of which varies according to the quantity of gold present. The precipitate is insoluble in *dilute acids;* the gold solution should be first mixed with the bichloride of tin, and the protochloride then added drop by drop. When the quantity of gold is extremely minute, a *pink tinge* pervades the solution.

256. "A very delicate method of applying this test is as follows:—*Sesquichloride of iron* is added to protochloride of tin until a permanent yellow colour is produced; the solution is then considerably diluted; the gold solution, having likewise been much diluted, is poured into a beaker, which is placed on a sheet of white paper; a glass rod is dipped into the tin-iron solution, and afterwards into the gold solution, when, if even a trace of the precious metal be present, a *blue or purple streak* will be observed in the track of the glass rod.

257. "This purple of Cassius test has the advantage of being applicable even in very acid solutions."—*Abel and Bloxam.*

258. PEROXIDE OF PLATINUM ($Pt O_2$).—This oxide is of a deep brown colour; its hydrate is reddish brown. Both the oxide and its hydrate dissolve readily in hydrochloric acid, but with difficulty in the oxygen acids. Persulphide of platinum ($Pt S_2$) is of a blackish brown colour.

259. *Chloride of potassium* or *ammonium* produces, in solutions of platinum, yellow crystalline precipitates of POTASSIO-CHLORIDE OF PLATINUM and AMMONIO-CHLORIDE OF PLATINUM. The presence of free hydrochloric acid promotes the formation of these

precipitates. Dilute solutions should be evaporated along with the chloride of potassium or ammonium and the free hydrochloric acid, on the water bath, to dryness, and the residue digested in weak spirit of wine until the excess of the alkaline chloride employed is dissolved.

260. Solutions of protochloride of tin produce, in solutions of binoxide of platinum, which contain much free hydrochloric acid, a dark *brown-red colour;* in exceedingly dilute solutions the colour is *yellow,* and becomes darker on standing. This test is a very delicate one for platinum. The dark brown colour is owing to the reduction of binoxide or bichloride of platinum to protoxide or protochloride.

SIXTH GROUP.

OXIDE OF SILVER.   PROTOXIDE OF MERCURY.   OXIDE OF LEAD.
  PEROXIDE OF MERCURY.   OXIDE OF BISMUTH.   OXIDE OF
  COPPER.   OXIDE OF CADMIUM.

261. The oxides of this group are insoluble in water. They all combine with nitric acid, forming soluble salts; many of them likewise form, with hydrochloric and sulphuric acid, soluble chlorides and sulphates; but a few give, particularly with the former acid, insoluble salts. This character permits of a sub-division of the group, which is fully exhibited under the head of its general properties.

262. In the state of sulphides they are insoluble, not only in the alkalies and alkaline sulphides, but likewise in the dilute mineral acids. They are therefore thrown down, both from their neutral, acid, and alkaline solutions, by sulphuretted hydrogen. They are all decomposed and rendered soluble in boiling *dilute* nitric acid, with the exception of PERSULPHIDE OF MERCURY.

263. The metallic radicals of these oxides possess the follow-

ing properties :—*Cadmium* decomposes water at a red heat, and at common temperatures in contact with strong acids. *Copper*, *lead*, and *bismuth*, absorb oxygen at a red heat; their oxides are therefore not decomposed by heat alone. They do not decompose water but at a very elevated temperature, and even then very feebly; neither do they decompose it in the presence of strong acids or bases. The affinity of *mercury* and *silver* for oxygen is very feeble: so much so, that their oxides are decomposed by heat alone, at a more or less elevated temperature. These metals do not decompose water, under any circumstances; they have therefore no tendency to rust when exposed to the air.

264. This group may, as before noticed, be divided into two sections :—

265. *a.* OXIDES which are precipitated by hydrochloric acid, viz., OXIDE OF SILVER, PROTOXIDE OF MERCURY, and OXIDE OF LEAD.

266. *b.* OXIDES which are not precipitated by hydrochloric acid, viz., PEROXIDE OF MERCURY, OXIDE OF BISMUTH, OXIDE OF CADMIUM, and OXIDE OF COPPER.

267. The slight solubility of chloride of lead in water renders it impossible to confine this member exclusively to the first section—a portion of the chloride, varying according to the amount of liquid present, always remaining dissolved. This is finally precipitated along with the members of the second section on the addition of hydrosulphuric acid. If attention be paid to the following facts, they will frequently remove a source of much confusion :—1. If lead has been discovered in the first section, a precipitate must always be obtained on passing hydrosulphuric acid through the filtrate, even if no other member of the group be present. 2. If only a small quantity of lead be present, hydrochloric acid may cause no precipitate, as a sufficient quantity of water may be present to dissolve the chloride formed. In this case, all the lead will be found in testing for the members of the second section.

TABLE VI.

BEHAVIOUR OF THE MEMBERS OF THE FIRST SECTION WITH THE SPECIAL REAGENTS.

Oxide of Lead (Pb O).	Oxide of Silver (Ag O).	Protoxide of Mercury (Hg₂ O).
P. 1. Chloride of Lead (Pb Cl) is difficultly soluble in *cold water*; it is much more soluble in *boiling water*. It is precipitated, by *sulphuric acid*, from its aqueous solutions, as insoluble SULPHATE OF LEAD (Pb O, SO₃).	Q. 1. Chloride of Silver (Ag Cl) is insoluble in *water*.	R. 1. Protochloride of Mercury (Hg₂ Cl) is insoluble in *water*.
P. 2. Chloride of Lead is very slightly soluble in *ammonia*; the ammoniacal solution becomes turbid after a short time, from the separation of the lead as an insoluble basic chloride (Pb Cl, 3 Pb O, + H O). This basic chloride is soluble in nitric acid; it is therefore easily distinguished from chloride of silver.	Q. 2. Chloride of Silver is easily soluble in *ammonia*. On the addition of any acid it is again precipitated from this solution.	R. 2. Protochloride of Mercury does not dissolve in *ammonia*, but becomes altered in colour, the *white chloride* being converted into a *black compound*.

BEHAVIOUR OF THE MEMBERS OF THE SECOND SECTION WITH THE SPECIAL REAGENTS.

Peroxide of Mercury (Hg O).	Oxide of Lead (Pb O).	Oxide of Bismuth (Bi O).	Oxide of Cadmium (Cd O).	Oxide of Copper (Cu O).
S. 1. Persulphide of Mercury (Hg S) is *black*; it is *insoluble* in boiling nitric acid, but is easily soluble in aqua regia.	T. 1. Sulphide of Lead is *black*; it is *soluble* in boiling nitric acid.	U. 1. Sulphide of Bismuth (Bi S) is *black*; it is *soluble* in boiling nitric acid.	V. 1. Sulphide of Cadmium is *yellow*; it is *soluble* in boiling nitric acid.	W. 1. Sulphide of Copper is *black*; it is *soluble* in boiling nitric acid.

	2. Sulphuric Acid	3. Ammonia	4. Carbonate of Ammonia
S.	S. 2. Sulphate of the peroxide of mercury is decomposed, in the presence of much water, into an insoluble basic and a soluble acid salt.	S. 3. *Ammonia** produces, in solutions of peroxide of mercury, a WHITE PRECIPITATE ($HgNH_2 + HgCl$), *insoluble* in an excess of the reagent.	S. 4. *Carbonate of Ammonia†* behaves in the same way, in solutions of peroxide of mercury, as caustic ammonia.
T.	T. 2. *Sulphuric Acid* precipitates, from solutions of lead, the SULPHATE (PbO, SO_3), which is *insoluble* in water and dilute acids.	T. 3. *Ammonia* throws down, from solutions of salts of lead, white basic salts, which are insoluble in an excess of the reagent.	T. 4. *Carbonate of Ammonia* precipitates, from solutions of lead, the CARBONATE ($PbOCO_2$), *insoluble* in an excess of the reagent.
U.	U. 2. *Sulphuric Acid* produces no precipitate in solutions of this oxide, SULPHATE of BISMUTH being *soluble* in water.	U. 3. *Ammonia* throws down, from solutions of bismuth, the HYDRATE, *insoluble* in an excess of the reagent.	U. 4. *Carbonate of Ammonia* throws down, from solutions of bismuth, a BASIC WHITE CARBONATE, *insoluble* in an excess of the reagent.
V.	V. 2. *Sulphuric Acid* produces no precipitate in solutions of this oxide, the SULPHATE being *soluble* in water.	V. 3. *Ammonia* precipitates, from solutions of cadmium, the HYDRATE, *soluble* in an excess of the reagent.	V. 4. *Carbonate of Ammonia* throws down, from solutions of cadmium, the CARBONATE (CdO, CO_2), *insoluble* in an excess of the reagent.
W.	W. 2. *Sulphuric Acid* produces no precipitate in solutions of this oxide, SULPHATE of COPPER being *soluble* in water.	W. 3. *Ammonia* produces, in solutions of this oxide, a GREENISH BLUE precipitate which *dissolves* with a beautiful azure colour in an excess of the reagent.	W. 4. *Carbonate of Ammonia* behaves in the same way in solutions of copper as caustic ammonia.

* The fixed alkalies precipitate all the members of this group from their solutions; the lead precipitate is difficultly soluble in an excess of the reagents; all the rest are insoluble. The precipitate produced by the fixed alkalies, in solutions of the peroxide of mercury, is the yellow hydrate, unless salts of ammonia are present; in that case the precipitate is the same as that produced by ammonia.

† The fixed alkaline carbonates precipitate all the members of this group from their solutions. If added to solutions of copper in the cold, they produce a basic carbonate; but if the solution is boiled, it is converted into the black oxide.

268. *First section.*—*Boiling water* being poured upon the precipitate produced by hydrochloric acid, will remove the CHLORIDE OF LEAD, if present, which is ascertained by *sulphuric acid* producing in the filtrate a precipitate of SULPHATE OF LEAD. If a residue remain after removing the chloride of lead by adding successively to the mixed chlorides fresh quantities of boiling water, until the last washings give on the addition of sulphuric acid no further precipitate, it proves that either chloride of silver or protochloride of mercury (calomel), or both, must be present. *Ammonia* being added to this residue, dissolves the CHLORIDE OF SILVER, whilst the CHLORIDE OF MERCURY is converted into a *black* compound. To detect the CHLORIDE OF SILVER in the ammoniacal solution, *nitric acid* must be added in excess, which, by destroying the solvent, causes the CHLORIDE OF SILVER (if present) to be reprecipitated.

269. *Second section.*—The precipitate produced by the general reagent, after being washed with distilled water until all trace of chlorine is removed, must be boiled in *dilute nitric acid*. If it all dissolves, with the exception of a light yellow mass of sulphur, PEROXIDE OF MERCURY is absent; but if, after boiling for some time, the undissolved mass presents a black appearance, it points out the probable presence of that member. Examine the black mass for peroxide of mercury as directed in par. 270. To the acid solution, after it has been filtered from the yellow or black mass and subsequently evaporated nearly to dryness, so as to remove the greater part of the free acid, must be added a little water, and then a few drops of *dilute sulphuric acid*, which will precipitate the LEAD as sulphate after the lapse of a longer or shorter time; the solution must therefore be allowed to stand some time before ammonia is added. *Ammonia* being added in excess to the filtrate, throws down the BISMUTH. The ammoniacal filtrate, after being slightly acidulated with acetic acid, must be divided into two

portious. To one portion is to be added *carbonate of ammonia** in excess, and heat applied; by this means the CADMIUM, if present, will be precipitated. COPPER is discovered, if it has not been already manifested by the blue colour of the ammoniacal solution, by *ferrocyanide of potassium* producing in the other portion of the acetic solution a brownish red-coloured precipitate.

270. If a black residue remain after boiling the mixed sulphides in nitric acid, it must be collected upon a filter, to separate it from the other members, and specially examined for peroxide of mercury by one of the two following methods:—1st. After having dried the black mass thoroughly, in a water bath, mix it with dry carbonate of soda, and proceed with the examination for mercury in the way described in par. 284. 2nd. Dissolve the black mass in as *small a quantity* of AQUA REGIA *as possible*, then add ammonia in slight excess, and then a slight excess of hydrochloric acid; examine the solution, thus prepared, for mercury, by means of copper wire, in the way described at par. 282.

271. *The following precautions must be attended to in analyzing this group:*—The means, both for separating and detecting the members of the first section, are so simple and positive, that no difficulty will be experienced by the student. It may nevertheless be as well to observe, that chloride of lead ought to be completely removed, before ammonia is added; for if it is not, a *white residue*, which is nothing more than chloride of lead, may remain after the addition of ammonia, when mercury is absent, which may perplex the student. And if the chloride of lead be not completely removed before the addition of ammonia, the ammoniacal solution will appear turbid, owing to the separation of an insoluble basic salt of lead; this will not, however, interfere with the test for silver, since it (the basic salt of lead) redissolves upon the addition of nitric acid. The difficulties which occur in examining the second section will be easily over-

* *See* Appendix B.

come by a little attention. Many erroneous conclusions will be formed if the simple yet necessary precaution of washing the sulphuretted hydrogen precipitate be neglected; because a small quantity of the hydrochloric acid employed to precipitate the first section, being left behind, will be converted, on the addition of nitric acid, into aqua regia, which, by dissolving the persulphide of mercury, may cause that member to be overlooked; and should the mercury thus pass into solution, a compound of that metal will be precipitated on the addition of ammonia, which may be mistaken for bismuth. The precipitate must therefore, before it is treated with nitric acid, be washed with water until the wash-water, acidulated with nitric acid, gives no precipitate with nitrate of silver. It is difficult to free the mass of sulphur, which separates on the addition of nitric acid, entirely from some of the undecomposed sulphides; and which, by communicating to it a black appearance, might lead to the belief that peroxide of mercury was present, even in the absence of that member. An experienced eye can generally distinguish between this mixture of undecomposed sulphide and sulphur, and persulphide of mercury, the former being light and flocculent, whilst the latter is dense and heavy; but a safe and legitimate conclusion can only be arrived at by examining it specially for mercury. A varying amount of sulphuric acid is always formed by dissolving the sulphides in nitric acid; a portion of the lead will therefore be precipitated as sulphate, and remain behind mixed up with the substance insoluble in nitric acid: it is necessary, on this account, to examine the insoluble mass for this member, if it should not be met with in its proper place. As sulphate of lead precipitates from dilute solutions, and especially from those which contain much free acid, only after the lapse of some considerable time; the solution ought, after the addition of sulphuric acid, to be allowed to stand for a considerable time (an hour) before adding the ammonia. A precipitate will be formed on the addition of

ammonia to the nitric solution, if either of these reagents contain a trace of iron, but this precipitate cannot be mistaken for bismuth if the following confirmatory test be applied:—Dissolve the precipitate obtained by ammonia in the least possible quantity of dilute hydrochloric acid, and evaporate just to dryness; redissolve the residue in water containing a drop of hydrochloric acid, and then add a large quantity of water; if a turbidness be produced, bismuth is present.

SPECIAL REMARKS.

273. OXIDE OF SILVER.—The colour of this oxide is brown. It is very soluble in nitric acid; it combines with ammonia, giving rise to a dangerous compound (fulminating silver). Many of the salts of silver are colourless and insoluble. The soluble ones do not affect vegetable colours, and are decomposed at a red heat. Many of them blacken on exposure to light; and they are all decomposed with the precipitation of metallic silver by many metals, such as *zinc*, *iron*, *copper*, etc., and other *reducing agents*. The principal minerals of this metal are the SULPHIDE (*silver glance* AgS), the CHLORIDE (*horn silver* AgCl), SULPHIDE OF SILVER and ARSENIC ($3\,Ag\,S + As\,S_3$), and SULPHIDE OF SILVER and ANTIMONY ($3\,Ag\,S + Sb\,S_3$); SILVER is also met with in the metallic state. It is likewise found in small quantities in most lead and copper ores.

274. When silver compounds, mixed with *carbonate of soda*, are subjected on charcoal to the inner blowpipe flame, brilliant metallic globules are produced, which are not attended with any incrustation.

275. OXIDE OF LEAD.—This oxide is of a yellow or reddish yellow colour. In commerce it frequently goes under the name of massicot, and when partially fused is called litharge. The hydrated oxide is of a white colour, and it speedily absorbs carbonic acid from the air. The best solvent, both for the oxide

and its hydrate, is nitric or acetic acid. The salts of lead are frequently insoluble, and are colourless, if the constituent acids be so. The soluble neutral salts redden litmus paper, and are decomposed at a red heat. The principal minerals of this metal are the SULPHIDE (*galena* or *lead glance* PbS) and the CARBONATE (PbO, CO_2).

276. *Chromate of potash* produces, in solutions of lead, a yellow precipitate of CHROMATE OF LEAD (PbO, CrO_3), soluble in the fixed alkalies, but insoluble in nitric acid.

277. When lead compounds, mixed with *carbonate of soda*, are exposed upon charcoal to the inner blowpipe flame, ductile metallic globules are formed, accompanied with an incrustation which is yellow whilst hot, but becomes paler on cooling.

278. PROTOXIDE or SUBOXIDE OF MERCURY.—This oxide is black; it is decomposed by heat, the mercury volatilizing in the metallic state. It forms no hydrate. The salts of the protoxide of mercury, when ignited, volatilize either with or without decomposition. The soluble neutral ones redden litmus paper; some of them are decomposed by much water into soluble acid and insoluble basic salts. The colour of the neutral salts is white, the colour of the basic ones is yellow. They are reduced, like the silver salts, by many metals, such as *zinc, iron, copper*, etc., and by other reducing agents.

279. To obtain the mercury from the protosalts of this metal, they may be decomposed either by copper, or protochloride of tin, or by means of carbonate of soda, in the way described at 282, 283, and 284.

280. PEROXIDE or OXIDE OF MERCURY.—This oxide is obtained in the form of a crystalline mass, nearly black whilst hot (at a red heat it is decomposed and entirely volatilized), but of a light red when cold. Its hydrate is yellow. Both the oxide and its hydrate are soluble in hydrochloric and nitric acid. The salts of the peroxide of mercury, when ignited, volatilize

either with or without decomposition. The soluble neutral ones redden litmus paper. The sulphate and nitrate are decomposed in the presence of much water into soluble acid and insoluble basic salts. The metals and other reducing agents which decompose the protosalts act in a similar manner upon the persalts of this metal.

281. These two oxides differ not only in colour, but likewise in their behaviour with alkalies and hydrochloric acid. The latter reagent is especially applicable for separating them, when they are present in the same solution; as protochloride of mercury (*calomel*) is insoluble, whilst the perchloride (*corrosive sublimate*) is soluble.

282. " Metallic copper, introduced into a solution of mercury, especially after acidification with hydrochloric acid, becomes covered with a white, lustrous coating; when moderately heated, the copper regains its original colour, vapours of mercury being evolved: this test is exceedingly delicate. Slips of copper wire, about an inch in length, may be used; they should be cleaned by shaking for a few moments with concentrated nitric acid, and thoroughly washed. Half a dozen such slips should be boiled for three or four minutes in the solution, previously acidulated with hydrochloric acid; they are then well rinsed, dried by pressure between blotting paper, and heated in a glass tube of $\frac{1}{4}$ inch diameter, constructed so as to allow the passage of a feeble current of air. A coating of minute *globules of mercury* is formed upon the cool part of the tube; these may be united into larger globules by rubbing with a glass rod."—*Abel* and *Bloxam*.

283. If protochloride of tin be added in small quantity to salts of the peroxide of mercury, it reduces them to the state of protoxide, and, as a consequence, white protochloride of mercury precipitating; but if it be added in excess, the salt of mercury (protosalts as well as persalts) is completely decomposed, metallic mercury being thrown down as a grey precipitate, which may be

united into globules by heat and agitation—but most readily by
boiling the metallic deposit, after decantation of the supernatant
fluid, with hydrochloric acid.

284. " Solid compounds of mercury, mixed with a large excess
(at least twelve parts) of *dry carbonate of soda*, and heated in a
perfectly dry tube of hard glass, having a diameter of about
$\frac{1}{4}$ inch, and expanded into a bulb at one end, furnish minute
globules of metallic mercury, which are deposited on the cool
part of the tube, and may be united into larger globules by
rubbing with a glass rod. This test is exceedingly delicate; in
order that it may be perfectly successful, the mercury compound
should be thoroughly dried (in a water bath), and the carbonate
of soda should be ignited immediately previous to use. In order
to prevent the sublimation of undecomposed mercury compounds,
it is well to cover the mixture in the bulb-tube with a layer
of pure carbonate of soda."—*Abel* and *Bloxam*.

The chief mineral of this metal is the PERSULPHIDE (*cinnabar*);
it is likewise met with in the metallic state.

285. OXIDE OF BISMUTH.—This oxide is of a yellow colour;
when heated, it acquires, for the time, a deeper tint; it fuses at a
red heat. Its hydrate is white. They are both readily soluble
in the dilute mineral acids. Most of the salts of bismuth are
decomposed at a red heat. They are colourless, provided the
constituent acid be so. The soluble neutral salts redden litmus
paper, and one distinguishing character which they possess is
that of being decomposed by water into soluble acid and inso-
luble basic salts. This property is exhibited in the most decided
manner by the chloride. To employ it as a confirmatory test,
dissolve the precipitate in a small quantity of hydrochloric
acid, evaporate nearly to dryness, and pour this solution into a
large quantity of water. If bismuth be present, a milky turbid-
ness will be produced. This metal is found principally in the
native state.

286. *Chromate of potash* throws down from solutions of bismuth the YELLOW CHROMATE. This salt differs from the corresponding one of lead by its solubility in dilute nitric acid, and its insolubility in potash.

287. When compounds of bismuth, mixed with *carbonate of soda*, are exposed on charcoal to the inner blowpipe flame, brittle metallic globules are obtained, attended with a yellow incrustation of oxide of bismuth.

288. OXIDE OF CADMIUM.—This oxide is of a brown or yellowish brown colour: its hydrate is white. They are both easily soluble in the dilute mineral acids. The salts of cadmium are colourless, provided the constituent acid be so. Most of them are soluble in water. The soluble neutral ones redden litmus paper, and are decomposed at a red heat. This metal occurs only in zinc ores. It is found as SULPHIDE in zinc blende, and as OXIDE or CARBONATE in calamine.

289. When compounds of cadmium, mixed with *carbonate of soda* or other reducing agents, are exposed on charcoal to the inner blowpipe flame, the charcoal becomes covered with a yellow or reddish yellow incrustation of oxide of cadmium.

290. OXIDE OF COPPER.—This oxide is black; its hydrate is of a light blue colour. They are both readily soluble in the dilute mineral acids. Most of the salts of this metal are soluble in water. The soluble ones redden litmus paper, and are decomposed at a red heat. In their anhydrous state, the salts are white; in their hydrated state they are of a blue or greenish blue colour, which their solutions exhibit, even when much diluted.

291. This metal is sometimes found in the native state; but it chiefly occurs in combination with sulphide of iron, constituting the COPPER PYRITES ($Cu_2 S + Fe_2 S_3$), and in BLUE COPPER ore, or MALACHITE ($2CuO, CO_2 + HO$).

292. Ferrocyanide of potassium throws down, even from dilute solutions of copper, a reddish brown precipitate of FERROCYANIDE

OF COPPER ($2Cu, Cfy$), which is insoluble in dilute acids, but is decomposed by the fixed alkalies.

293. If bright *metallic iron* be introduced into a solution of a salt of copper, it becomes coated with a red deposit of that metal, provided the solution be neutral or only very slightly acid.

294. When any of the compounds of copper, mixed with *carbonate of soda*, are exposed on a charcoal support to the inner blowpipe flame, METALLIC COPPER is obtained, unaccompanied with any incrustation on the charcoal.

CHAPTER III.

THE GENERAL PROPERTIES OF THE BASIC GROUPS.

295. It will be seen by consulting the general table (7), that some of the reagents produce a precipitate with more than one of the groups; the analysis must therefore be commenced by removing those substances the general reagent of which produces no precipitate with the members of any other group under the same circumstances. Such a course will be adopted, if the reagents are employed in the order observed in the table.

296. FIRST DIVISION OF THE SIXTH GROUP.—The analysis must be commenced by adding to the solution *hydrochloric acid*, which precipitates the members of the first section of the sixth group when they are present. When a precipitate is produced, collect it upon a filter, wash it twice with cold water, and then examine it, according to the first section of table 6, and par. 268. The wash-water must be collected with the filtrate. *Before adding the hydrochloric acid, consult* pars. 303, 304, and 305.

297. SECOND DIVISION OF THE SIXTH, AND THE WHOLE OF THE FIFTH GROUP.—To the filtrate from the precipitate produced by hydrochloric acid, or to the solution with which it has failed to give a precipitate, is to be added *sulphide of hydrogen* gas*

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* If the oxides of silver and lead, and protoxide of mercury, had not to be sought for, we must nevertheless add hydrochloric acid to the solution to render it acid, before adding sulphide of hydrogen, in order to prevent the members of the third and fourth groups from being precipitated by that reagent, and to ensure the complete precipitation of the fifth group.

(hydrosulphuric acid), until the solution smells strongly of the gas after it has been shaken and gently warmed for some time; the remaining members of the sixth and all the members of the fifth group, when present, will be precipitated. When a precipitate is produced, collect it upon a filter and wash it with hot water until the wash-water is no longer acid to test-paper; the wash-water need not be collected with the filtrate, but may be thrown away. *Boiling caustic soda* must be poured upon the washed precipitate : the alkali dissolves out the members of the fifth group; whilst the members of the sixth group, being insoluble in the alkali, remain behind upon the filter. If a portion of the precipitate should be insoluble in the caustic soda, it must, after being well washed with hot water, be examined for the members of the second division of the sixth group according to table 6 and par. 269. To the caustic soda solution must be added hydrochloric acid in excess. If a precipitate is produced on the addition of the acid to the alkaline solution, the colour of which is *white*, this arises merely from the separation of sulphur, none of the members of the fifth group being present; if the precipitate possess a *yellow* or *orange colour*, ANTIMONY, BINOXIDE OF TIN,* and ARSENIC, can only be present. If the colour of the precipitate is *black*, then all the members of the group must be sought for. The analysis of the precipitate, after being well washed with hot water, must be conducted according to the directions given under the fifth group (205). *Before passing the sulphide of hydrogen gas through the solution, consult* pars. 306, 307, and 308.

298. THE FOURTH GROUP.—If the directions given in the previous paragraph have been obeyed, the solution, which has now to be examined for the fourth group, will have a strong odour of sulphide of hydrogen; if they have not been obeyed, *they must be* before proceeding to examine the solution for this or the

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* The colour of protosulphide of tin is a blackish brown.

following groups. The filtrate from the sulphide of hydrogen precipitate, or the solution with which it has failed to give a precipitate, must be boiled until every trace of sulphide of hydrogen is expelled. To ascertain when all the gas is expelled, hold a piece of bibulous paper, moistened with a solution of some soluble salt of lead, over the boiling liquid: when the lead paper does not alter in colour, all the sulphide of hydrogen is expelled. If boiling the liquid causes a separation of sulphur, the solution, after the sulphide of hydrogen is expelled, must be filtered to free it from the sulphur; a very small portion of the liquid must then be examined for protoxide of iron by ferricyanide of potassium. When iron is present, the rest of the solution, to which no ferricyanide of potassium has been added, must be boiled with a few drops of nitric acid until all the iron is converted into sesquioxide,[*] which is accomplished when a drop of the solution does not give a blue colour with ferricyanide of potassium. To the solution, when the iron is peroxidized, must be added *chloride of ammonium and ammonia;* the ammonia must be added until the solution, after it has been well shaken, smells of the volatile alkali. Nitric acid need not be added to the solution when it contains no iron, but the chloride of ammonium and ammonia can at once be added to it after it has been freed from the sulphide of hydrogen and sulphur. Warm the solution after the addition of the ammonia; and when a precipitate is produced, showing the presence of one or all of the members of the fourth group, collect it upon a filter, wash it with hot water until the wash-water does not turn red test-paper blue; examine it then according to table 4 and pars. 170, 171, 172, & 173. *Before adding the chloride of ammonium and ammonia, consult* pars. 309, 310, 311, &c.

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[*] When the fifth and sixth groups are not sought for, but we commence the analysis by examining for the members of the fourth group, we must not neglect to convert the iron, when any of it exists as protoxide, into sesquioxide, by boiling the solutions with nitric acid.

TABLE VII.—Behaviour of the Basic Groups

FIRST GROUP.	SECOND GROUP.		THIRD GROUP.
Potash (KO), Soda (Na O), Ammonia (N H₄ O).	*First Subdivision.* Baryta (Ba O), Strontia (Sr O), Lime (Ca O).	*Second Subdivision.* Magnesia (Mg O).	Oxide Manganese (MnO), Oxide of Zinc (ZnO), Oxide of Cobalt(CoO), Oxide of Nickel (Ni O), Protoxide of Iron (Fe O)
1. Hydaochloric Acid *does not* precipitate the members of this group from their solutions, because *their Chlorides are soluble*	1. Hydrochloic Acid *does not* precipitate the members of this group from their solutions, because *their Chlorides are soluble.*		1. Hydrochloric Acid *does not* precipitate the members of this group from their solutions, because *their Chlorides are soluble.*
2. Hydrosulphuric Acid *does not* precipitate the members of this group, either from their neutral acid or alkaline solutions, because *their Sulphides are soluble.*	2. Hydrosulphuric Acid *does not* precipitate the members of this group, either from their neutral acid or alkaline solutions, because *their Sulphides are soluble.*		2. Hydrosulphuric Acid *does not* precipitate the members of this group from their *acid* solutions, because *their Sulphides* are soluble in *dilute acids*, even in the cold.
3. Ammonia *does not* precipitate either of the other two members of the group.	3. Ammonia *does not** precipitate the members of this division from their solutions.	3. Ammonia *precipitates* Magnesia *partly* from its solutions, as *Hydrate* (Mg O, H O); the presence of *Salts of Ammonia prevents** the precipitation *altogether.*	3. Ammonia *precipitates* the members of this group as *Hydrates.* In an excess of the reagent, the Hydrates of Zinc, Nickel, and Cobalt are *readily soluble*, but the Hydrates of Manganese and Protoxide of Iron are *insoluble*; but the presence of *Salts of Ammonia prevents* the precipitation of the *Manganese* and *Oxide of Iron.*
4. Sulphide of Ammonium *does not* precipitate the other two members of this group from their solutions, because *their Sulphides are soluble.*	4. Sulphide of Ammonium *does not* precipitate the members of this group from their solutions, because *their Sulphides are soluble.*		4. Sulphide of Ammonium *precipitates* all the members of this group from neutral and alkaline solutions, as *Sulphides.*
5. Carbonate of Ammonia *does not* precipitate either of the other two members of this group from their solutions.	5. Carbonate of Ammonia *precipitates* the members of this division from their solutions as *Carbonates*; the presence of *Salts of Ammonia does not interfere* with the precipitation.	5. Carbonate of Ammonia *precipitates* Magnesia *only partly*, and the presence of *Salts of Ammonia prevents* the precipitation *altogether.*	5. Carbonate of Ammonia *precipitates* all the members of this group; but they *are all*, with the exception of Manganese and Oxide of Iron, *readily soluble* in an *excess* of the reagent.
6. Arseniate of Ammonia *does not* precipitate either of the other two members of this group from their solutions.	6. Arseniate of Ammonia *precipitates* the members of this division from their neutral and alkaline solutions, as *Arseniates.*	6. Arseniate of Ammonia *precipitates* Magnesia from its neutral & alkaline solutions, as *Arseniate*; violent agitation promotes the formation of the precipitate. The precipitate is more soluble in *hot* than *cold* water.	6. Arseniate of Ammonia *precipitates* the members of this group from their neutral solutions, as *Arseniates.*

* The phosphates and oxalates of baryta, strontia, and lime, and phosphate of magnesia, are soluble in dilute mineral acids, but insoluble in water and the alkalies; consequently, when their acid solutions are rendered neutral or alkaline by ammonia, *these salts* are precipitated; therefore when baryta, strontia, and lime are in combination with phosphoric and oxalic acids, and when magnesia is in combination with phosphoric acid, they are precipitated in combination with these acids by ammonia, from their acid solutions, along with the members of the fourth group

FOURTH GROUP.	FIFTH GROUP.	SIXTH GROUP.	
		Second Subdivision.	*First Subdivision.*
ALUMINA (Al_2O_3), SESQUIOXIDE CHROMIUM (Cr_2O_3), SESQUIOXIDE OF IRON (Fe_2O_3).	ARSENIOUS ACID (AsO_3), ARSENIC ACID (AsO_5), TEROXIDE OF ANTIMONY (SbO_3), OXIDE OF TIN (SnO), BINOXIDE OF TIN (SnO_2), TEROXIDE OF GOLD (AuO_3), BINOXIDE OF PLATINUM (PtO_2).	OXIDE OF LEAD (PbO), BINOXIDE OF MERCURY (HgO_2), OXIDE OF BISMUTH (BiO), OXIDE OF CADMIUM (CdO), OXIDE OF COPPER (CuO).	OXIDE OF SILVER (Ag PROTOXIDE OF MERC (HgO), OXIDE OF L (PbO).
1. HYDROCHLORIC ACID *does not* precipitate the members of this group, because *their Chlorides are soluble.*	1. HYDROCHLORIC ACID *does not* precipitate the members of this group, because *their Chlorides are soluble.*	1. HYDROCHLORIC ACID *does not* precipitate the members of this division of the group, because *their Chlorides are soluble.*	1. HYDROCHLORIC A *precipitates* the memb of this division of group, because *t Chlorides* are insolu Chloride of Lead slightly soluble in wa it is more soluble in than cold water.
2. HYDROSULPHURIC ACID *does not* precipitate any of the members of this group from their acid solutions, because *Sulphide of Iron* is readily soluble in acids, and the *Sulphides of Aluminum* and Chromium are not formed in the humid way	2. HYDROSULPHURIC ACID *precipitates* all the members of this group from their acid solutions, as *Sulphides.*	2. HYDROSULPHURIC ACID *precipitates* all members of this group from their neutral al line and acid solutions, as *Sulphides.*	
3. AMMONIA, *even in the presence of its Salts,* precipitates the members of this group as *Hydrates,** which an *excess* of the reagent *does not* redissolve.	3. AMMONIA *precipitates* some of the members of this group.	3. AMMONIA precipitates the members of group; but *in an excess* of the reagent, the o *of Silver, Cadmium,* and *Copper* redissolve rea the *rest* are *insoluble* in an excess of the reage	
4. SULPHIDE OF AMMONIUM *precipitates* all the members of this group from neutral and alkaline solutions; Sesquioxide of Iron, as *Protosulphide;* Alumina and Sesquioxide of Chromium, as *Oxides.*	4. SULPHIDE OF AMMONIUM, *if added in excess,* does not precipitate the members of this group from their solutions, because *their Sulphides* are soluble in the *Alkaline Sulphides.*	4. SULPHIDE OF AMMONIUM *precipitates al* members of this group from their neutral alkaline solutions, as *Sulphides.*	
5. CARBONATE OF AMMONIA *precipitates* all the members of this group from their solutions, as *Oxides:* an *excess* of the reagent *does not* redissolve them.	5. CARBONATE OF AMMONIA precipitates *some* of the members of this group, as *Oxides.*	5. CARBONATE OF AMMONIA *precipitates* al members of this group from their solutions: an excess of the reagent *does not* redissolve t with the *exception* of Copper.	
6. ARSENIATE OF AMMONIA *precipitates* the members of this group from their neutral solutions, as *Arseniates.*	6. ARSENIATE OF AMMONIA *precipitates* some of the members of this group from their neutral solutions, as *Arseniates.*	6. ARSENIATE OF AMMONIA *precipitates* members of this group from their neutral tions, as *Arseniates.*	

* When phosphate of iron and phosphate alumina are present in a solution, they are precipitated as phates, and not as Hydrates, by ammonia.

399. THE THIRD GROUP.*—To the filtrate from the precipitate produced by ammonia, or to the solution with which it has failed to give a precipitate, is to be added *sulphide of ammonium* in the cold.† If any of the members of the third group are present, a precipitate will be produced by the sulphide of ammonium. When a precipitate is produced, collect it upon a filter, and, after washing it well with hot water, examine it according to table 3 and par. 149, if the precipitate is of a *light colour*; but if it is *black*, par. 150. Before filtering the whole of the solution, when a precipitate is produced by sulphide of ammonium, add to that portion of the liquid which has been filtered a little more sulphide of ammonium; if the reagent produces a further precipitate, add some to the unfiltered as well as to the filtered portion, then filter it, and again test the filtrate with sulphide of ammonium. If the sulphide of ammonium cause no precipitate in the filtered liquid, proceed with the filtration, as the group has been completely precipitated. *Before adding any sulphide of ammonium to the solution, consult* pars. 311, 312, & 313.

300. FIRST DIVISION OF THE SECOND GROUP.—To the filtrate from the precipitate produced by the sulphide of ammonium, or to the solution with which it has failed to give a precipitate, is to be added *carbonate of ammonia;*‡ the solution must then be gently warmed for some time, but not boiled. If one or all of

* Although protoxide of iron belongs, on account of its general properties, to this group, we have placed it in the special table of the fourth group; because, in separating the groups, it is converted by nitric acid into sesquioxide—a member of the fourth group: we have thought it advisable, therefore, to contrast its special properties with those of the fourth.

† When the student does not look for the members of the three previous groups, viz., the sixth, fifth, and fourth, he must, before adding sulphide of ammonium to the solution, add chloride of ammonium and ammonia: in other words, he must add them to the solution which he has to examine for the members of the third group, if they (*i.e.*, chloride of ammonium and ammonia) have not been added in the previous course of the analysis. The chloride of ammonium is added, to prevent the precipitation of the magnesia by the ammonia.

‡ When the student does not look for the members of the four previous groups, viz., the sixth, fifth, fourth, and third, he must, before adding the

the members of this division are present, a precipitate will be produced by the carbonate of ammonia, especially after warming the solution. When a precipitate is produced, collect it upon a filter, wash it with hot water, and afterwards examine it according to table 2 and pars. 122, 123, 124, or 125. *Before adding the carbonate of ammonia, consult* pars. 314 and 315.

301. SECOND DIVISION OF THE SECOND GROUP.—The filtrate from the carbonate of ammonia precipitate must be tested with a little more carbonate of ammonia before we attempt to look for magnesia. If on the further addition of carbonate of ammonia a precipitate is produced, it must be filtered; the precipitate must be examined, along with the previous precipitate, for baryta, strontia, and lime, and the filtrate must be again tested with carbonate of ammonia. The filtrate from the carbonate of ammonia precipitate, or the solution with which it has failed to give a precipitate, must be divided into two parts. To one part of the solution must be added *arseniate of ammonia:** the liquid, after the addition of the reagent, ought to be shaken very violently; and if, after time (one or two hours) has been allowed for the formation of the precipitate, no precipitate should appear, this part of the

carbonate of ammonia to the solution, add chloride of ammonium and ammonia: in other words, he must add them to the solution which he has to examine for the members of the second group, if they (*i. e.*, chloride of ammonium and ammonia) have not been added in the previous course of the analysis. The chloride of ammonium is added to prevent the precipitation of the magnesia by the carbonate of ammonia; any ammoniacal salt may be employed, the acid of which forms no insoluble compound with magnesia or the other members of the group. The carbonate of ammonia employed being generally a sesqui-carbonate, a portion of the alkaline earths is apt to be dissolved by the excess of carbonic acid. The ammonia is added to prevent this: it does so by converting the sesquicarbonate into a neutral carbonate.

* When the student does not look for the previous groups and the first section of this group, he must, before adding the arseniate of ammonia to the solution, add chloride of ammonium and ammonia. The chloride of ammonium is added to prevent the precipitation of the magnesia by the ammonia. The ammonia is added because arseniate of magnesia and ammonia is less soluble in water containing ammonia than in pure water.

solution can be thrown away. The solution must be quite cold when the arseniate of ammonia is added, as the arseniate of magnesia and ammonia is more soluble in hot than cold water. The other part of the solution must be examined for potash and soda in the way pointed out in the next paragraph. When arseniate of ammonia produces a precipitate in one part of the solution, the two portions of the solution must be mixed together; a further quantity of arseniate of ammonia must be added; the liquid, after the addition of the reagent, must be shaken very violently; and, after time has been allowed for the complete precipitation of the magnesia, the liquid must be filtered. To the filtrate must be added a little more arseniate of ammonia; if this should cause a further precipitate, the solution must be again filtered and the filtrate again tested with arseniate of ammonia. The excess of the arsenic acid must be got rid of in the filtrate before we can test for the non-volatile alkalies. When, therefore, the filtrate gives no further precipitate with arseniate of ammonia, sulphide of ammonium containing an excess of sulphur* must be added in sufficient quantity, and the solution evaporated to one half its bulk; hydrochloric acid must then be added, slightly in excess, and the solution filtered from the precipitated sulpharsenic acid $(As\ S_5)$. The filtrate must then be examined for potash and soda in the way described in the following paragraph. *Before adding the arseniate of ammonia, consult* par. 316.

302. The First Group.—The second portion of the solution in which magnesia has been found to be absent, and the filtrate from the sulpharsenic acid precipitate (when magnesia has been present in the solution under examination), are each examined in the following way for potash and soda:—The solution is evaporated to dryness, and ignited until all fuming has ceased. As a slight

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* To obtain sulphide of ammonium containing an excess of sulphur, heat some of the ordinary sulphide of ammonium with some flowers of sulphur; filter the solution if all the sulphur does not dissolve, and use the filtrate.

quantity of the ammoniacal salt frequently becomes detached from the sides of the vessel during the process of ignition—however long the ignition may be continued, it will remain unvolatilized, as it does not become sufficiently heated. It is necessary, therefore, after all fuming has ceased, to remove the lamp, allow the vessel to cool, and, when cold, to wash down from the sides of the vessel any unvolatilized ammoniacal salt with the smallest possible quantity of water; the liquid must then be evaporated, and the ignition continued until all fuming ceases. During the ignition, the dry matter frequently assumes a black or brown colour; this is owing to the ammoniacal salts, which have been added during the course of the analysis, containing organic matter. Should this black matter not be destroyed during the ignition, it will be got rid of on dissolving the residue which remains after the expulsion of the ammoniacal salts in water, and filtering the solution; the organic matter, being rendered insoluble by the heat, will remain behind upon the filter. After all the ammoniacal salts have been expelled, *as much boiling water* as would fill a small-sized thimble should be poured into the vessel, in order to dissolve the fixed alkalies if they are present. The liquid must then be filtered through a very small filter, and the clear filtered liquid examined for potash and soda according to par. 100; and par. 102 ought to be consulted. We always look for ammonia in a portion of the original solution. *Before examining for the alkalies, consult* par. 317.

PARTICULAR OBSERVATIONS REGARDING THE PRECIPITATES PRODUCED BY THE GENERAL REAGENTS, AND THE PRECAUTIONS TO BE ATTENDED TO IN EXAMINING THE SOLUTIONS.

303. *Precautions to be attended to in examining for the first section of the Sixth Group.*—Before adding hydrochloric acid to any solution under examination, it is necessary to ascertain, by

test-papers, whether the solution is acid, neutral, or alkaline. When it is one of the two former, a few drops of the acid will generally be sufficient; if alkaline, the acid must be added until it is decidedly in excess. When a precipitate is produced, add the acid, drop by drop, until it ceases to increase; then add a few drops more, shake the mixture, and filter. When no precipitate is produced, a few drops of the acid will in most cases be sufficient, since our only object in adding it, then, is to acidify the solution, in order to prevent the precipitation of the members of the third and the members of the fourth group by sulphide of hydrogen. *When an evolution of gas takes place on the addition of the hydrochloric acid, consult* par. 322.

304. As oxide of silver is not precipitated, under certain circumstances, by hydrochloric acid—and as a precipitate may be produced on the addition of hydrochloric acid, in the absence of the oxides of silver, lead, and protoxide of mercury—it is requisite to notice, 1st, the substances which interfere with the precipitation of the oxide of silver; 2nd, the substances which may be precipitated, and under what condition the precipitation takes place. 1st. When pernitrate of mercury is present in the solution, oxide of silver, if present, will not be precipitated by the hydrochloric acid, because chloride of silver is soluble in a solution of pernitrate of mercury, especially if the solution is hot and concentrated: upon the addition of water, and cooling, the solution may deposit shining yellowish white crystals, which are pure chloride of silver. When pernitrate of mercury is suspected to be present, acetate of ammonia ought to be added to the solution after the addition of the hydrochloric acid, as this ensures the complete precipitation of the chloride of silver. 2nd. The precipitate* may be occasioned by the presence of some salt of antimony or

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* If the hydrochloric acid employed contain a trace of sulphuric acid, and baryta be present in the fluid under examination, a slight trace of insoluble sulphate of baryta will be formed, which may be distinguished by the difficulty experienced in separating it from the fluid by filtration.

bismuth, as the chlorides of these metals are decomposed by much water into soluble acid and insoluble basic salts. This precipitate[*] may also arise from the presence of some substance insoluble in water, but soluble in the caustic, carbonated, or sulphuretted alkalies, or in an alkaline cyanide—for example, phosphate of alumina, or alumina dissolved in caustic soda, sulpharsenious acid dissolved in carbonate of ammonia, tersulphide of antimony dissolved in an alkaline sulphide, cyanide of nickel dissolved in an alkaline cyanide; or the precipitate may be due to silicic acid, some alkaline silicate being present. If the precipitate is due either to antimony or bismuth, it will redissolve on the addition of a few drops more of hydrochloric acid. When silicic acid is the substance thrown down, the precipitate will appear very gelatinous, and will remain undissolved on the further addition of acid; a fresh portion of the original solution must therefore be acidulated with nitric acid, and evaporated to dryness to render the silicic acid insoluble; the ignited mass may then be digested with dilute nitric acid, and filtered.[†] The analysis of the filtrate must then be conducted in the regular way, by adding to it hydrochloric acid, &c. If the precipitate should be due to the presence of any of the other substances, a fresh portion of the original solution ought to be taken, and nitric acid added to it until it is decidedly acid. If the precipitate does not disappear on the addition of the acid, the solution ought to be warmed; if this should fail to dissolve the precipitate, it must be collected upon a filter, and examined as a substance insoluble in water and acids (*see* 551). The analysis of the solution or filtrate must then be conducted in the regular way, by adding to it hydrochloric acid, &c.

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[*] Hydrochloric acid precipitates, of the inorganic acids, boracic acid; and of the organic acids, benzoic and uric acids. If the solution is very concentrated, the two former are dissolved by hot water, and the uric acid by heating with nitric acid.

[†] The precipitate left upon the filter must be examined for silicic acid according to the method described under the head of that acid (*see* par. 405).

305. As the chlorides of lead, silver, and protochloride of mercury, are very heavy, they easily separate from the solution; there is therefore no need to warm the fluid to effect this object. Indeed it would be disadvantageous to do so, as a portion of the protochloride of mercury would be converted into perchloride, and the greater portion if not all the chloride of lead would be dissolved.

306. *Precautions to be observed in examining for the second section of the Sixth and the whole of the Fifth Group.*—Before passing sulphide of hydrogen through the solution, it will be necessary to dilute it with water, if it be very acid, as many of the sulphides will not readily precipitate from very acid solutions. Should the liquid, on being diluted, become turbid, it arises from the presence of some salt of antimony or bismuth. A few drops of acid will redissolve this precipitate. Arsenic acid is precipitated, with very great difficulty, by sulphide of hydrogen. When this substance is present, the addition of sulphurous acid,* assisted by a gentle degree of heat, reduces it to a lower oxide (arsenious acid). This must be done before passing sulphide of hydrogen through the solution; for not only is the arsenic acid precipitated with difficulty, but if oxide of zinc is also present in the solution, the precipitate produced by the sulphide of hydrogen is not pure sulpharsenic acid, but a compound of that acid and sulphide of zinc, having the following composition (ZnS, AsS_5)— so that if the oxide of zinc and arsenic acid were present in equivalent proportions, all the zinc would be precipitated along with the arsenic acid by sulphide of hydrogen. If, however, the arsenic acid be first reduced, by means of sulphurous acid, to the state of arsenious acid, then no sulpharsenic acid is

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* If baryta, strontia, or oxide of lead, be present, the sulphurous acid will give rise to a precipitation of these oxides, as sulphates; the precipitate should be collected upon a filter, washed, dried, and then examined as a substance insoluble in water and acids, according to 551, &c.

preeipitated, but only sulpharsenious acid (AsS_3); and sulphide of zinc is not precipitated along with this last acid.

307. If, on the addition of hydrosulphuric acid, no precipitate be produced, it proves the absence of the remaining members of the sixth and all the members of the fifth group. If a precipitate be produced, the colour of which is white,* this likewise proves the absence of these groups, as the white precipitate is merely due to a separation of the sulphur, occasioned by the reduction of some higher oxide to a lower degree of oxidation. If the colour of the solution, originally orange or yellow, change to a green, after the gas is passed through it, the separation of sulphur is due to the reduction of chromic acid to the state of sesquioxide of chromium; the white sulphur suspended in the green solution frequently perplexes the student, as it appears at first like a green precipitate. If the separation of sulphur be not attended with any change in colour, it is (probably) attributable to the reduction of the sesquioxide of iron to the state of protoxide: chromic acid and sesquioxide of iron being both found in their lowest degree of oxidation, after sulphide of hydrogen, or any other reducing agent, has been added to their solutions.

308. If on the first transmission of sulphide of hydrogen through the solution a *white* precipitate be formed, which, on a further addition of the reagent, acquires *an orange colour*, and becomes finally *black*, it points out that some salt of the peroxide of mercury is present. If the precipitate, on its first formation, assumes a red or brownish red colour, and becomes finally black, it indicates the probable presence of some salt of lead.

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* If nitric be present in the solution, a thick, tenacious yellow mass of sulphur will separate, occasioned by the decomposition of the sulphide of hydrogen by the acid. When such is the case, the gas has to be passed through the solution for some time before its characteristic odour will be imparted to the liquid, showing that a sufficient quantity has been added. Chloric acid and free chlorine decompose sulphide of hydrogen in the same way as nitric acid.

309. *Precautions to be observed in examining for the Fourth Group.*—If the sulphide of hydrogen were not expelled before boiling the solution with nitric acid, the latter might give rise, by oxidation of the sulphur, to sulphuric acid, which would precipitate baryta and strontia, and possibly lime, as sulphates, if they were present. Even when nitric acid has not to be added to the solution, no iron being present, it is necessary to expel the sulphide of hydrogen before adding ammonia, otherwise sulphide of ammonium would be formed when the ammonia was added, and consequently the third as well as the fourth group would be precipitated. When the solution is very acid, no chloride of ammonium need be added, as a sufficient amount of ammoniacal salt will be formed on the addition of the ammonia.

310. When much sesquioxide of chromium is present, a small quantity will frequently dissolve in the ammonia, and will impart to the fluid a puce-red tint. When this occurs, it is difficult to remove the last traces of chromium from the solution. If warming the solution fail, it is better to disregard it; for if the solution were evaporated to effect the object, a greater or less quantity of the oxides of manganese, nickel, and cobalt, if they were present, would be precipitated.

311. The precipitate produced by ammonia may consist, in addition to the members of the fourth group, of the following salts:—Alumina, sesquioxide of iron, baryta, strontia, lime, and magnesia, when in combination with phosphoric acid; and baryta, strontia, and lime, when in combination with oxalic acid. When the student looks for acids as well as bases, he must examine the precipitate produced by ammonia, according to table 5. Baryta, strontia, and lime, when in combination with hydrofluoric and boracic acids, may also be precipitated by ammonia in minute quantities; but as a sufficient quantity of the bases will always remain in solution, and be precipitated in their proper place, and as the acids will be found in the

examination for acids, we have not included these salts in the table.

311. *Precautions to be observed in examining for the Third Group.*—If chromic acid and baryta are both present in a solution, a substance insoluble in acids is sometimes found on dissolving the precipitate produced by ammonia, or that produced by sulphide of ammonium; the insoluble substance is sulphate of baryta. A sulphur acid appears to be formed when chromic acid is reduced by sulphide of hydrogen, which becomes converted into sulphuric acid after some time.

312. The precipitate produced by sulphide of ammonium is very difficult to filter: the filtrate will frequently come through the filter *turbid* for some time; there is no remedy for this but to pass it through the filter until it is perfectly clear. The student must not mistake between a *turbid filtrate* and one which is *perfectly clear but coloured.* A filter can only remove what is held in suspension by a liquid, as in the first case; it cannot remove what is dissolved, as in the second case: when the filtrate is coloured, consult the next par. The precipitate must be carefully washed with water containing a little sulphide of ammonium, in order to prevent the precipitated sulphides from oxidizing. If the wash-water comes through of a deep brown colour, it must be treated as directed in the next par.

313. If the filtrate from the sulphide of ammonium precipitate be of a very dark brown colour, it is occasioned by the presence of nickel, the sulphide of that metal being slightly soluble in sulphide of ammonium. When a considerable portion of this substance has passed into solution, the filtrate, and likewise the wash-water if it is dark-coloured, must be evaporated until the excess of sulphide of ammonium is expelled; the solution is then acidified with dilute hydrochloric acid, and the black precipitate which separates on the addition of the acid collected upon a filter, and examined with that previously obtained.

314. *Precautions to be observed in examining for the first division of the Second Group.*—After the addition of the carbonate of ammonia, the solution should be heated gently but not boiled, since the chloride of ammonium might then decompose and dissolve the carbonates of the alkaline earths.

315. Although carbonate of ammonia does not precipitate completely baryta, strontia, and lime from their solutions, especially when the quantity of the salts of ammonia present is considerable, it is sufficiently exact for all ordinary qualitative purposes. " The separation is never perfect, owing to the solvent action which salts of ammonia exercise, more especially upon carbonate of baryta and lime; indeed, minute traces of baryta and lime can rarely be precipitated in this manner. Baryta is separated the most completely by sulphuric acid or a sulphate; lime, by oxalate of ammonia, in presence of ammonia and some chloride of ammonium; strontia, same manner as lime, or by ammonia and carbonate of ammonia in presence of chloride of ammonium."

316. *Precautions to be observed in examining for the second division of the Second Group.*—If the solution has become very dilute during the course of the analysis, it will render the detection of the magnesia more certain, if, before adding the arseniate of ammonia, the solution is concentrated. In any case time must be allowed for the formation of the precipitate, and the solution must be quite cold when the reagent is added.

317. *Precautions to be observed in examining for the First Group.*—The precautions to be observed in examining for the first group are few but important. The student must be perfectly certain, before he attempts to test for potash and soda, particularly the former, that all the ammoniacal salts are expelled; after expelling the ammoniacal salts, he must dissolve the residue in as small a quantity of water as possible—as much as would fill a small thimble is sufficient in all cases, unless there is an ex-

tremely large quantity, which he can at once see by the amount of residue. He must allow the potash time to precipitate, as, when small quantities are present, it only appears after some hours. If any of the salts of the bases, which are insoluble in potash, are present, a precipitate will be produced on adding potash or soda to the original solution to test for ammonia. This precipitate will not, of course, interfere in the least with the detection of ammonia: the student proceeds in the same way as if no precipitate had been produced. For further precautions the student is referred to the first group.

CHAPTER IV.

THE GENERAL PROPERTIES OF THE ACIDS.

318. All acids belong to one of two grand classes, which are distinguished by the terms *Organic* and *Inorganic*.

319. The striking characteristic of the organic class of acids is the separation of charcoal which attends their decomposition by heat, along with the conversion of the bases with which they were combined (if alkalies or alkaline earths) into carbonates.

320. Acids do not admit of that accurate classification into groups which is the case with bases, many of them being members of more than one group.

INORGANIC ACIDS.

321. The inorganic acids treated of in the present work are divided into six groups.

322. *First Group.*—The acids in this division are not only gaseous in their free state, but their affinity for bases is likewise feeble; their salts are therefore decomposed by most acids, the decomposition being attended with *effervescence*, owing to the liberated acid assuming the gaseous state. On this account they are always discovered at the very commencement of an analysis; for an evolution of gas must take place, when hydrochloric acid is added to test for the first section of the sixth group of bases, if these acids are present. The evolved gas must be examined—1, By the smell; 2, by paper moistened with a solution of acetate of lead; 3, by placing the thumb on the mouth of the test-tube,

so that the gas may accumulate, and finally decanting it (taking care not to allow any of the liquid to pass over along with it) into another test-tube half filled with *lime water*. If, on agitating the liquid, a precipitate be formed, CARBONIC ACID is present. The special properties just alluded to will be found detailed in the respective paragraphs of these acids.

323. Positive proof will thus be afforded of the presence or absence of carbonic and hydrosulphuric acid. Hydrocyanic acid may, especially in the presence of much hydrosulphuric acid, be overlooked in this way. The methods to be employed for its detection in all cases will be afterwards stated.

324. *Second Group.*—The acids contained in this group are detected in testing for the bases. ARSENIOUS and ARSENIC ACID, being precipitated by hydrosulphuric acid, are classed amongst the bases; whilst the remaining acid is converted into a lower oxide, sesquioxide of chromium, which is one of the members of the fourth group of bases. The change of colour attending this decomposition is so characteristic, that it cannot be overlooked by the most inexperienced student. The only thing which can cause the least difficulty or perplexity is the mistaking a green solution, with a light-coloured precipitate suspended in it, for a green precipitate.

325. *Third Group.*—It will be seen, by referring to the table, that some of the acids already noticed form a part of this group. The examination is commenced by adding to a portion of the original solution *chloride of barium;* if a precipitate be formed which is not entirely soluble in hydrochloric acid, SULPHURIC ACID is present; filter off from the insoluble sulphate of baryta, and to the filtrate add ammonia; if no precipitate ensue, the other acids (boracic acid excepted) in the group cannot be present. Borate of baryta is soluble in ammoniacal salts, from which solution it is not precipitated on the addition of ammonia. Arseniate and arsenite of baryta are likewise soluble in ammoniacal salts, from which solutions ammonia fails to precipitate

them, but their presence or absence will have been determined already. If any base is present, which is precipitated by ammonia, it must be removed before we can employ the alkali for pointing out whether any other acid is present but sulphuric.

326. All the baryta salts mentioned in the table are colourless, with the exception of the CHROMATE, which is of a *pale yellow colour*.

327. *The following precautions must be attended to in examining for this group of acids:*—The first thing which claims attention is the state of the solution, viz., whether it be acid, alkaline, or neutral. When it is acid, ammonia must be added until it is slightly alkaline; should this cause a precipitate, filter off, and to the filtrate add chloride of barium; if no precipitate ensue on the addition of ammonia, add at once the baryta salt. Should the solution be alkaline, the alkalinity proceeding from one of the fixed alkalies, it would be better to neutralize with hydrochloric acid before adding the chloride of barium. Nitrate of baryta must be substituted for chloride of barium, and the precipitate produced be digested with nitric acid, when lead, silver, or protoxide of mercury are present. The precipitate must not be digested in undiluted acids, because chloride of barium and nitrate of baryta are insoluble in concentrated acids, and would therefore separate from the solution. When carbonic acid is present in the solution, it is better to get rid of it before adding the baryta salt; this is effected by adding to the solution hydrochloric acid, and boiling for a short time. When all the acid has been removed, add ammonia to neutralize the solution, and finally the baryta salt.

328. *Fourth Group.*—This group is merely a section of the last. The examination is commenced by adding to a portion of the original solution *chloride of calcium;* the precipitate produced by this reagent, after being collected upon a filter and washed, must be digested with acetic acid. If complete solution ensue, HYDROFLUORIC ACID and OXALIC ACID are both (probably) absent.

If the precipitate does not dissolve (or at least, not entirely), filter, and to the filtrate add one drop of sesquichloride of iron. If a precipitate be formed, it points out the probable presence of PHOS-PHORIC ACID; should no precipitate be formed, that acid is probably absent. A special examination must be made in all cases for BORACIC ACID, OXALIC ACID, and HYDROFLUORIC ACID.

329. *The precautions to be attended to* are very similar to those given in the third group. The same plan must be pursued when the solution is acid or alkaline. Nitrate of lime must also be employed when silver, lead, or protoxide of mercury are present. When carbonic acid is present, it is better to get rid of it before adding the reagent. When much sulphuric acid is present, the solution ought to be diluted with water before adding the chloride of calcium, to prevent any sulphate of lime from precipitating. Arsenious and arsenic acids are precipitated by chloride of calcium from neutral solutions free from ammoniacal salts. When these acids are present, avoid the precipitation of their lime salts by adding chloride of ammonium along with the chloride of calcium. Borate of lime, like borate of baryta, is soluble in ammoniacal salts, from which solution it is not precipitated on the addition of ammonia: the non-formation therefore of a precipitate by chloride of calcium does not prove the absence of boracic acid, if ammoniacal salts are present.

330. *Fifth Group.—Nitrate of silver* precipitates, along with most of the acids previously noticed, the non-metallic elements CHLORINE, BROMINE, IODINE, and the compound body CYANOGEN, from their combinations with hydrogen and the metals.

331. To a portion of the original solution must be added *nitrate of silver.* If a precipitate be produced, it must be digested with nitric acid, which will dissolve all the silver salts, with the exception of the CHLORIDE, CYANIDE, BROMIDE, and IODIDE OF SILVER. WHEN THE SILVER PRECIPITATE does not completely dissolve in nitric acid, wash the insoluble portion, so as to free it from all

soluble silver salts, then add *ammonia*, and gently heat the mixture: the CHLORIDE, CYANIDE, and BROMIDE OF SILVER, being soluble in that reagent, will dissolve, whilst the IODIDE OF SILVER, being insoluble, will remain undissolved. When the silver precipitate does not completely dissolve in the ammonia, filter the mixture and add to the filtrate nitric acid in excess. If no precipitate is formed on the addition of the nitric acid, chlorine, bromine, and probably cyanogen, are absent. If a precipitate is formed, before proceeding to examine it further, test the original solution specially for cyanogen, either by the Prussian blue test (412), or by sulphide of ammonium (414); or, if peroxide of mercury has been discovered in testing for the bases, by the method described in par. 415.

332. WHEN CYANOGEN IS ABSENT, the silver precipitate, soluble in ammonia and insoluble in nitric acid, can only be due to bromine or chlorine, or both. The analyst must now test specially for bromine in the original solution: *when iodine is absent*, he can test the original solution at once for bromine, by the method described in par. 418; *when iodine is present*, it must be removed from the solution before an examination can be made for bromine. To effect this object, the analyst must add to the original solution a very slight excess of carbonate of soda, then a mixture of solutions of sulphate of copper and sulphate of iron (429), until the whole of the iodine is precipitated: subsequently filter, and to the filtered liquid add a slight excess of carbonate of soda; again filter, and test the filtrate for bromine, as directed at 418. *When bromine is absent*, the silver precipitate, soluble in ammonia and insoluble in nitric acid, can be due to the presence of chlorine only; *when bromine is present*, a special examination must be made for chlorine in the original solution, in the way described in par. 408.

333. WHEN CYANOGEN IS PRESENT, the silver precipitate, which has been thrown down from the ammoniacal solution by nitric acid, must, after it has been well washed by decantation, be transferred to a porcelain crucible, dried, and then ignited so as to decompose

the cyanide of silver; and the residue, afterwards, must be boiled with dilute nitric acid. *If the residue does not dissolve, or at least not entirely, in the nitric' acid*, it points out the presence of bromine or chlorine, or both: examine for them in the original solution, in the way described in the preceding paragraph. *If it all dissolves in the* nitric acid, bromine and chlorine are absent. Add to the nitric acid solution, when the ignited residue dissolves, or to the filtrate, when it does not entirely dissolve, hydrochloric acid ; if a precipitate of chloride of silver is produced, it confirms the presence of cyanogen.

334. Some of the acids give with solutions of silver characteristic coloured precipitates. Thus CHROMATE OF SILVER is *red ;* SULPHIDE OF SILVER, *black ;* ARSENIATE OF SILVER, *red ;* SILICATE OF SILVER, *yellow* or *white ;* ARSENITE, PHOSPHATE, and IODIDE OF SILVER, *yellow.* The rest of the acids give, with soluble silver salts, colourless precipitates.

335. *The following precautions must be attended to in analyzing this group.*—The solution must be perfectly neutral *to testpaper :* an acid one is neutralized by adding ammonia slightly in excess, and then boiling the solution until all free alkali has been expelled. When a soluble sulphide or free hydrosulphuric acid is present, it is necessary, before testing with nitrate of silver, to remove the sulphur compound by adding nitric acid and warming the solution. When sulphate of the protoxide of iron is present, the silver salt will be reduced, metallic silver being precipitated. This may be obviated by converting the iron into peroxide: to effect this, boil the solution with a few drops of nitric acid.

336. The presence of the different acids, which the general reagents *chloride of barium, chloride of calcium,* and *nitrate of silver,* have pointed out as existing in the solution, must be confirmed by the *special tests.*

337. *Sixth Group.*—A *special* examination must always be made for the acids contained in this group.

TABLE VII.

BEHAVIOUR OF THE INORGANIC ACIDS WITH THE GENERAL REAGENTS.

ACIDS WHICH ARE GASEOUS AT THE COMMON TEMPERATURE AND PRESSURE.

CARBONIC ACID, HYDROSULPHURIC ACID, HYDROCYANIC ACID.

These acids are liberated from their combinations by the *stronger acids*; being set free, they immediately assume the gaseous state. The decomposition of their salts by acids is therefore attended with *effervescence*.

ACIDS WHICH ARE DECOMPOSED BY SULPHURETTED HYDROGEN.

ARSENIOUS ACID, ARSENIC ACID, CHROMIC ACID.

ARSENIOUS and ARSENIC ACID are converted by *sulphuretted hydrogen* into the corresponding SULPHUR ACIDS, viz., SULPHARSENIOUS and SULPHARSENIC ACID, which are insoluble in the dilute mineral acids. Their presence or absence is therefore proved in testing for the bases—they in fact form a part of the fifth group.

CHROMIC ACID is converted, by the action of the *same reagent*, into a LOWER and BASIC OXIDE (sesquioxide of Chromium), which belongs to the fourth group. The change of colour which attends this decomposition is very characteristic, viz., the conversion of a *yellow* or *orange coloured* solution to a *green* one; the reduction is likewise attended with a separation of sulphur.

ACIDS WHICH ARE PRECIPITATED FROM A NEUTRAL SOLUTION BY CHLORIDE OF BARIUM OR ANY SOLUBLE SALT OF BARYTA.

CARBONIC ACID, ARSENIOUS ACID, CHROMIC ACID, ARSENIC ACID, SULPHURIC ACID, BORACIC ACID, PHOSPHORIC ACID, OXALIC ACID, HYDROFLUORIC ACID, SILICIC ACID.

The salts which these acids form with baryta are *all soluble* in hydrochloric acid, with the exception of *sulphate of baryta*; the solubility or insolubility of the baryta precipitate in acids is at once characteristic of the *presence or absence* of SULPHURIC ACID.

TABLE VII.—*continued.*

ACIDS WHICH ARE PRECIPITATED FROM A NEUTRAL SOLUTION BY CHLORIDE OF CALCIUM OR ANY SOLUBLE LIME SALT.

BORACIC ACID, PHOSPHORIC ACID, OXALIC ACID, HYDROFLUORIC ACID.

PHOSPHATE of LIME and BORATE of LIME are soluble in *acetic acid*, whilst OXALATE of LIME and FLUORIDE of CALCIUM are insoluble.

ACIDS WHICH ARE PRECIPITATED FROM A NEUTRAL SOLUTION BY NITRATE OF SILVER.

HYDROSULPHURIC ACID, ARSENIOUS ACID, ARSENIC ACID, CHROMIC ACID, BORACIC ACID, PHOSPHORIC ACID, OXALIC ACID, SILICIC ACID.

ACIDS WHICH ARE PRECIPITATED BOTH FROM A NEUTRAL AND ACID SOLUTION BY NITRATE OF SILVER.

HYDROCHLORIC ACID, HYDROCYANIC ACID, HYDROBROMIC ACID, HYDRIODIC ACID.

The silver salts of these acids are soluble in *ammonia*, with the exception of IODIDE of SILVER.

ACIDS WHICH ARE NOT PRECIPITATED BY ANY REAGENT.

NITRIC ACID, CHLORIC ACID.

The salts of these acids *deflagrate* on ignited charcoal.

SPECIAL TESTS FOR THE INORGANIC ACIDS.

338. The special tests must be applied to the original solution; a separate portion must be taken for each acid.

339. CARBONIC ACID.—This acid is distinguished from the other gaseous acids by giving a precipitate with lime water; the way for evolving the gas, when combined, and testing it, when liberated, with lime water, is described in par. 356.

340. SULPHIDE OF HYDROGEN. — This acid is distinguished from the other gaseous acids by giving, with soluble salts of silver and lead, black precipitates; the way for applying the test is described in par. 361. The sulphur in sulphides which are not decomposed by hydrochloric acid, but require for their decomposition nitric or nitro-hydrochloric acids, cannot be detected in this way: recourse must be had in these cases to the process described in par. 363.

341. HYDROCYANIC ACID.—This acid can be distinguished from all other acids by the tests described in pars. 412 and 414; if, however, peroxide of mercury has been discovered in testing for the bases, the process described in par. 415 must be employed.

342. ARSENIOUS ACID, ARSENIC ACID, CHROMIC ACID.—As these acids are discovered in testing for the bases, no experiments require to be made for their detection when testing for the acids.

343. SULPHURIC ACID.—The presence or absence of this acid is ascertained on testing a part of the solution with the general reagent, chloride of barium; no further test is needed to prove its absence or presence.

344. BORACIC ACID. — This acid can be detected, in most cases, by the method described in par. 376; but the most certain test is the one described in par. 377.

345. PHOSPHORIC ACID.—When the phosphates are soluble in ammoniacal solutions (and the student can decide this when he

knows what bases are present), this acid can be detected by the method described in par. 382; but the most certain tests are 385 and 386, especially the last. The student must, however, remember that arsenic acid gives precipitates with these reagents, similar to those given by phosphoric acid. When arsenic acid is present, it must, on this account, be removed from the solution by sulphide of hydrogen, or be reduced to the state of arsenious acid, before testing for phosphoric acid.

346. OXALIC ACID. — This acid is detected by the method described at 393; but very minute quantities of it are more securely detected by boiling the substance with a solution of carbonate of soda, for some time; subsequently filtering, and the filtrate acidifying with acetic acid, and then adding to it a solution of sulphate of lime (392).

347. HYDROFLUORIC ACID.—Test for this acid, when silicic acid is absent, by the method described at 395; when silicic acid is present, by the one described at 397 or 398.

348. SILICIC ACID.—To test for this acid, evaporate the solution to dryness with an acid, and proceed as directed at 402 or 403.

349. HYDROCHLORIC ACID.—When hydrocyanic acid and hydrobromic acid are absent, the presence of this acid is proved by the insolubility of the silver precipitate in nitric acid, and by its solubility in ammonia; when hydrocyanic acid is present, and hydrobromic acid absent, its presence is proved, if, after igniting the silver precipitate, which is insoluble in nitric acid but soluble in ammonia, a whitish residue remains, which is insoluble in nitric acid. When hydrobromic acid is present, no matter whether hydrocyanic acid is present or absent, the presence of hydrochloric acid can only be ascertained by the test described at 408.

350. HYDROBROMIC ACID.—When hydriodic acid is present, it must first be precipitated, by the solutions of copper and iron (429), from the liquid, before we can test for bromine; when this

has been accomplished, the test described at 418 can be applied. In the absence of iodine, this test for bromine can be applied at once to the original solution.

351. HYDRIODIC ACID.—Iodine is best discovered by the test described at 428.

352. NITRIC ACID.—The tests described at 433 and 434 are the most characteristic of this acid.

353.—CHLORIC ACID.—The presence or absence of this acid is proved by the tests described at 439 and 440.

CARBONIC ACID. (CO_2).

354. This acid exists at the common temperature and pressure as a colourless, inodorous, and non-inflammable gas. Being heavier than the atmosphere in the proportion of 1·5 to 1, it can be decanted from one vessel to another like a liquid. It reddens blue litmus paper, previously moistened with water, which after a time returns to its original colour, owing to the acid having volatilized. It is soluble in *cold* water, but when the solution is heated the gas escapes.

355. The neutral alkaline carbonates are the only *neutral* salts of this acid which are soluble in pure water. The carbonates are decomposed by all free acids soluble in water (hydrocyanic and hydrosulphuric acids excepted), with evolution of carbonic acid.

356. *To detect* carbonic acid, add to the solution or solid substance under examination *hydrochloric acid;* and warm the solution, if sufficient gas for detection cannot be procured without. Should any gas be evolved, allow it to accumulate by placing the thumb on the mouth of the test-tube, and afterwards decant it (taking care not to allow any of the liquid to pass over along with it) into another test-tube half filled with *lime water.* A white precipitate of CARBONATE OF LIME will be produced, if carbonic acid is present.

357. Many of the insoluble carbonates dissolve in water containing free carbonic acid—from which solutions they are precipitated on boiling, the free acid being expelled. It is in this state that most of the lime and magnesia in spring and river waters exist. The incrustations which are formed in the vessels in which such waters are boiled are due to the precipitation of these carbonates occasioned by the removal of the free carbonic acid. Carbonic acid is best detected in waters by adding to them *lime water;* by this means not only is the CARBONATE OF LIME which is formed precipitated, but also that which pre-existed in the solution. This process is employed on a large scale for softening hard waters (waters impregnated with earthy matter).

358. All the carbonates, with the exception of those of the alkalies, lose their acid upon ignition, the metal being left either in an oxidized or uncombined state, according to its greater or less affinity for oxygen. The alkaline carbonates and bicarbonates affect test-paper in the manner of a free alkali.

359. *The following precautions must be attended to in testing* for *this acid:*—When the substance is in the solid state, it should be reduced to fine powder; and a little water should be added prior to the acid, to displace the air in its pores, otherwise an apparent effervescence will ensue from the expulsion of air. In the case of alkaline carbonates, the decomposing acid must be added until the solution reddens blue litmus paper—that is, until the acid is in *excess;* otherwise, the carbonic acid set free may combine with some of the undecomposed carbonate, forming with it a bicarbonate, no effervescence consequently taking place. No decomposition takes place on the addition of strong nitric acid to carbonate of baryta, especially the native carbonate, because nitrate of baryta is insoluble in the strong acid. Water must therefore be added, as well as the acid, for the decomposition to be effected in this and many other cases.

HYDROSULPHURIC ACID (*Sulphuretted Hydrogen* H S).

360. This acid exists at the common temperature and pressure as a colourless inflammable gas, possessing a highly offensive odour resembling that of rotten eggs. It burns with a blue flame, the products of combustion being sulphurous acid and water. It is soluble in water, three volumes of which dissolve one volume of the gas; this solution reddens litmus paper. On exposing the gas in a state of solution to the air, it is decomposed, water being formed, and sulphur in a highly divided state being separated.

361. Most metallic sulphides dissolve with decomposition in *hydrochloric acid*, in which case SULPHURETTED HYDROGEN is evolved, which, from its characteristic smell, is easily recognized. When the quantity is so minute that the smell fails to afford a sufficient proof, it may be detected by holding a piece of paper moistened with a solution of any soluble SALT OF LEAD over the mouth of the test-tube, as a brown or black coating of SULPHIDE OF LEAD will be formed upon the paper.

362. When sulphides are dissolved in *nitric* or *nitro-hydrochloric* acid, SULPHURIC ACID is formed along with a separation of sulphur, which may be recognized by its colour, and also its behaviour upon ignition. In the case of sulphides, therefore, which, from their insolubility in hydrochloric acid, must be dissolved in nitric or nitro-hydrochloric acids, the sulphur is converted into *sulphuric acid*, and not given off as sulphuretted hydrogen.

363. To ascertain whether the sulphur existed in an unoxidized state, when nitric or nitro-hydrochloric acid has been employed as the solvent of the substance under examination, a small portion of the *original* substance, in fine powder, must be fused with a little solid hydrate of potash or soda, in a platinum spoon, by means of the blowpipe flame. The fused mass must then be dissolved in a little water and filtered; a bright strip of

silver (or polished coin) is put into the solution, and the fluid warmed.   If a sulphide were present, a brownish black film of sulphide of silver would form upon the metal.   This film may be removed afterwards by rubbing the metal with leather and quicklime.

364. When the sulphides of the heavy metals are heated in contact with air, sulphurous acid is evolved : the metal being left in some cases uncombined, and in others as an oxide.   The sulphides of the alkalies and alkaline earths are converted by this process into sulphates.   As the student is made familiar, in passing through the basic groups, with the properties of the various sulphides, their solubility or insolubility in water, the alkalies, and the various acids, their colour, &c., it is unnecessary to notice them here.

Chromic Acid (CrO_3).

365. Chromic acid is a solid coloured acid occurring in the form of beautiful crimson needles, which deliquesce rapidly when exposed to the air, the solution possessing a deep red-brown tint.   This acid is decomposed, upon ignition, into sesquioxide of chromium and oxygen.   All its salts are coloured; the neutral chromates possessing a yellow, and the acid or bichromates a red colour.   Most of the salts are insoluble in water; they are nearly all soluble in nitric acid.

366. Chromic acid, whether in its free or combined state, is reduced by *hydrosulphuric acid* to the state of SESQUIOXIDE OF CHROMIUM; water and some oxide of sulphur is formed in this decomposition, along with a separation of sulphur.   The change of colour which attends this decomposition, viz., the conversion of a yellow or red coloured solution to a green one, is so characteristic that it cannot be mistaken.

367. Alkaline chromates may be prepared from insoluble chromates by fusing the latter in conjunction with alkaline carbonates.

368. When testing for the bases, we always find the chromic acid as sesquioxide of chromium, since hydrosulphuric acid reduces it to that state.

SULPHURIC ACID (*Oil of Vitriol*) (HO, SO_3).

369. Anhydrous sulphuric acid (SO_3) is a white feathery crystalline mass, which, when exposed to the air, emits dense white fumes. It is destitute of acid properties until it has combined with water and passed into the hydrated state. The hydrated acid is a heavy, colourless, oily fluid, which possesses a strong affinity for water, producing, when mixed with it, a great degree of heat. Its affinity for water is so great, that it decomposes organic substances when placed in contact with them, removing their hydrogen and oxygen, whilst the carbon is left behind as a black coaly mass, a portion of which dissolves in the acid and communicates to it a brown tint. If heat is applied, the carbon is oxidized at the expense of the sulphuric acid, carbonic acid and sulphurous acid being formed: these facts may be illustrated by pouring some strong sulphuric acid upon white sugar. Sulphuric acid, at temperatures below its boiling point (572 F), displaces all other acids from their combinations with bases, but above that temperature it is itself displaced by the non-volatile acids.

370. Most of the sulphates, with the exception of the sulphates of baryta, strontia, and lead, are soluble in water. The alkaline sulphates and the three just named are the only salts of this acid which are not decomposed on simple ignition.

371. Sulphates in dilute solutions containing organic matter are gradually converted into sulphides. Water containing a sulphate may therefore, after it has been kept a long time in a bottle or any closed vessel, be found to contain sulphuretted hydrogen, although originally it was perfectly free from that gas.

372. Sulphate of baryta, *from its insolubility in acids*, is at once distinguished from all the other baryta salts; any *soluble salt*

of baryta is therefore the best and most delicate test for SUL-PHURIC ACID.

373. Insoluble sulphates are completely decomposed by fusion with *alkaline carbonates*, an ALKALINE SULPHATE being produced along with a CARBONATE or an OXIDE of the METAL.

374. When a sulphate, mixed with *charcoal* and *carbonate of soda*, is fused upon a charcoal support by the inner blowpipe flame, sulphide of sodium is produced. If the fused mass, moistened with water, be placed upon a piece of silver, a brown stain of sulphide of silver will be formed.

BORACIC ACID (BO_3).

375. This acid is best obtained by adding to a boiling concentrated solution of biborate of soda (borax) strong sulphuric acid, until the liquor becomes sour to the taste: on cooling, the greater part of the boracic acid separates from the solution in the form of colourless crystalline scales, containing water. When ignited, they fuse to an anhydrous glassy mass, which, on exposure to the air, absorbs water, swells, and becomes opaque. This acid, in the anhydrous state, is a colourless fixed glass, fusible at a red heat. The hydrate ($2BO_3, 3HO$) is a porous white mass; in the crystalline state ($2BO_3, 3HO + 3$ aq.) it presents small scaly laminæ. The hydrated acid is much more soluble in hot than cold water. When an alcoholic or an aqueous solution of this acid is evaporated, a portion of the acid volatilizes with the vapours of the solvent, but alone it is perfectly fixed at a red heat. One peculiar property which this acid possesses is that of affecting turmeric paper in the manner of a free alkali; it acts, however, upon blue litmus paper like other acids. All the borates, with the exception of the alkaline ones, are almost totally insoluble in pure water; they dissolve readily in acids, and in water containing ammoniacal salts. They are not decomposed upon ignition: they are colourless, and all of them, *even the acid salts*, manifest an alkaline reaction.

376. An alcoholic solution of boracic acid burns with a *green-coloured flame*, which becomes more distinct upon stirring the mixture.   To detect a borate, add to the substance under examination *strong sulphuric acid* and *alcohol* or *wood naphtha ;* ignite the mixture subsequently.   If a borate be present, the borders of the flame will appear *green*, which becomes more distinct upon stirring, and the delicacy is further increased by repeatedly extinguishing and rekindling the flame.   The only substance which at all interferes with this test is copper, the salts of which impart the same colour to the flame.   This metal, if present, must therefore be got rid of by sulphuretted hydrogen, before testing for boracic acid.

377. A solution of one part of borax in one thousand parts of water, acidified with hydrochloric acid, imparts to turmeric paper, after drying, a distinctly brown tint (II. Rose).   This method may therefore be employed in place of the usual method for the detection of boracic acid.   The slip of paper ought only be dipped *half* into the fluid, and it ought to be dried at a *gentle* heat.

Phosphoric Acid $(3 \ HO, \ PO_5)$.

378. Anhydrous phosphoric acid (PO_5) appears under the form of white flakes, which rapidly absorb moisture from the atmosphere.   It has a great affinity for water, with which it combines in three different proportions, forming three distinct acids, which have the following constitution—

> Tribasic phosphoric acid $(3 \ HO, \ PO_5)$.
> Bibasic phosphoric acid $(2 \ HO, \ PO_5)$.
> Monobasic phosphoric acid $(HO, \ PO_5)$.

379. Each of these acids forms, with bases, a distinct class of salts.

380. The tribasic acid, which is the most important, is the only one treated of in this work.   It appears in the form of

colourless crystals, which deliquesce rapidly in the air. When strongly heated in an open platinum vessel it volatilizes without a residue.

381. The neutral phosphates, with the exception of the alkaline ones, are nearly all insoluble in water. The action of heat converts the tribasic phosphates into bibasic or monobasic salts, according to the number of atoms of basic water expelled.

382. *Sulphate of magnesia,* or *any soluble magnesian salt,* produces in aqueous solutions of the phosphates, if concentrated, a white precipitate of PHOSPHATE OF MAGNESIA (2 MgO, HO, PO_5). A salt much more insoluble in water is produced by adding *chloride of ammonium, ammonia,* and then the *magnesian salt;* in this way PHOSPHATE OF MAGNESIA AND AMMONIA (2 MgO, NH_4O, PO_5) is precipitated, which is slightly soluble in pure water, but almost insoluble in water containing ammonia. In dilute solutions it only appears *after much agitation and the lapse of some time;* agitation promotes its formation in all cases. This test can only be applied when the phosphates are soluble in ammoniacal solutions.

383. *Acetate of lead* produces a white precipitate of PHOSPHATE OF LEAD (3 PbO, PO_5), which is soluble in nitric acid. If this precipitate, after being dried, is heated in the outer flame of the blowpipe, it becomes distinctly crystalline on cooling. This test is very characteristic, not only on account of the crystalline structure of the bead, but also from the circumstance that the phosphate of lead is the only salt of that metal which is not reduced to the metallic state when heated in the inner blowpipe flame. It is evident that, to render this test of any value, the phosphate of lead must be freed thoroughly, by washing, from all acetate of lead.

384. *Nitrate of silver* throws down, both from solutions of phosphates containing one or two atoms of fixed base, as well as from phosphates containing three atoms of fixed base, a light yellow precipitate of phosphate of silver (3 AgO, PO_5), which is

readily soluble in nitric acid and in ammonia. If the solution contained a phosphate containing three atoms of fixed base, the fluid in which the precipitate is suspended will manifest a neutral reaction, whilst the reaction will be acid if the solution contained a phosphate containing one or two atoms of fixed base. The acid reaction is occasioned by the nitric acid receiving, for the three equivalents of oxide of silver which it yields to the phosphoric acid, only 2 or 1 eq. of fixed base, and 1 or 2 eq. of water ; and as the latter does not neutralize the acid properties of the nitric acid, the solution becomes acid. Monobasic and bibasic phosphate of silver is white; consequently, a tribasic phosphate, containing 1 or 2 eq. of fixed base, yields, after ignition, a white precipitate with nitrate of silver (AgO, PO_5, or 2 AgO, PO_5).

385. "If to a solution containing phosphoric acid and the *least possible excess* of hydrochloric or nitric acid a tolerably large amount of acetate of soda is added, and then a drop of *sesquichloride of iron*, a yellowish white flocenlent-gelatinous precipitate of PHOSPHATE OF SESQUIOXIDE OF IRON is formed. An excess of sesquichloride of iron must be avoided, as acetate of sesquioxide of iron (of red colour) would thereby be formed, in which the precipitate is not insoluble. This reaction is of importance, as it enables us to detect the phosphoric acid in phosphates of the alkaline earths: to effect the complete separation of the phosphoric acid from the alkaline earths, a sufficient quantity of sesquioxide of iron is added to impart a reddish colour to the solution, which is then boiled (whereby the whole of the sesquioxide of iron is thrown down, partly as phosphate, partly as basic acetate), and filtered hot. The filtrate contains the alkaline earths as chlorides. If you wish to detect, by means of this reaction, phosphoric acid in presence of a large proportion of sesquioxide of iron, boil the hydrochloric acid solution with sulphite of soda until the sesquichloride is reduced to protochloride, which reduction is indicated by the decoloration of the solution: add carbonate of

soda, until the fluid is nearly neutral; then acetate of soda, and finally, one drop of sesquichloride of iron. The reason for this proceeding is, that acetate of protoxide of iron does not dissolve phosphate of sesquioxide of iron.

386. "If some *molybdate of ammonia* is mixed in a test-tube with hydrochloric or nitric acid, in sufficient quantity to redissolve the precipitate which forms at first, and a little of a very dilute fluid containing phosphoric acid is then added, and the mixture boiled, the fluid acquires an intensely yellow colour, and after some time a yellow precipitate separates, which is insoluble in hydrochloric acid. The exact composition of this precipitate is not yet ascertained; we only know that it contains MOLYBDIC ACID, AMMONIA, and a little PHOSPHORIC ACID. This reaction is so delicate that the phosphoric acid may be detected by its means in almost all salts and most minerals containing it. As the yellow compound is decomposed by free phosphoric acid, an excess of the fluid containing the phosphoric acid must be carefully avoided. The yellow precipitate may, when it has subsided, be perceived even in dark-coloured fluids.

387. "In phosphate of alumina the phosphoric acid may be detected also by one of the two following methods:—

388. "Add carbonate of soda to the hydrochloric acid solution until the free acid is nearly neutralized; mix with carbonate of baryta in excess; add solution of soda or potash, and boil. This process gives the alumina in solution, the phosphoric acid in a precipitate of phosphate of baryta. Dissolve this precipitate in hydrochloric acid, decompose by sulphuric acid, filter, and test the filtrate with sulphate of magnesia, with addition of chloride of ammonium and ammonia.

389. "Mix the hydrochloric acid solution with tartaric acid: add ammonia in excess; and finally, to the clear solution, chloride of ammonium and sulphate of magnesia. If a precipitate forms only after some time, this cannot be considered a safe indication

of the presence of phosphoric acid, as, under the circumstances named, a precipitate of tartrate of magnesia, resembling the phosphate of magnesia and ammonia, may form in a solution of the proper degree of concentration, though no phosphoric acid is present. The precipitate must therefore be tested for phosphoric acid, which is done by dissolving it in nitric acid, evaporating the solution, with addition of some pure nitrate of potash or soda, to dryness, igniting the residue, then heating with hydrochloric acid, filtering the solution, and mixing the filtrate with ammonia in excess. The formation of a crystalline precipitate of phosphate of magnesia and ammonia confirms the presence of phosphoric acid."—*Fresenius.*

Oxalic Acid (HO, C_2O_3, or HO, $\overline{O}$).

390. Oxalic acid crystallizes from its aqueous solutions in four-sided prisms. These crystals contain three atoms of water, of which one is essential (HO, $C_2O_3 + 2$ aq.). When warmed, the two atoms of non-essential water (water of crystallization) are given off, and the hydrate of oxalic acid remains as a white powder, which melts at 350°, and, when further heated, sublimes—a portion, however, being decomposed. It is very soluble in water, and highly poisonous. It is usual to place it in the list of organic acids; but since its salts, upon ignition, leave no carbonaceous residue, it has been included in the list of inorganic acids.

391. All the oxalates are decomposed at a red heat, the oxalic acid being resolved into carbonic acid and carbonic oxide. If the base with which the acid is combined be an alkali or an alkaline earth, it is left as a carbonate; the other bases are left either in an oxidized or metallic state, according to their greater or less affinity for oxygen.

392. *Lime water* and all the soluble *salts of lime* produce in solutions of oxalic acid and the oxalates, even if highly

diluted, a white precipitate of OXALATE OF LIME, which is insoluble in acetic acid.

393. When *concentrated sulphuric acid* is added to dry oxalic acid or an oxalate, it withdraws the constitutional water in the one case and the base in the other from the anhydrous acid (C_2O_3), which, being incapable of existing alone, splits up into CARBONIC ACID and CARBONIC OXIDE. The two gases escape with effervescence; and if a light be applied as they issue from the mouth of the tube, the latter will burn with a blue flame.

HYDROFLUORIC ACID (HF).

394. This acid is best obtained by the action of concentrated sulphuric acid on fluoride of calcium (fluor spar). The powdered mineral is gently heated with the acid in a retort of lead, and the acid condensed in a receiver of the same metal. It is obtained in the form of a very volatile liquid, strongly acid and corrosive, fuming in the air. It burns the skin like red-hot iron, causing a sore which is not easily healed. It is distinguished from all other acids by dissolving insoluble silicic acid and the silicates which are insoluble in the other acids; on this account it cannot be prepared or kept in glass vessels.

395. " If a finely pulverized fluoride, no matter whether soluble or insoluble, is heated in a platinum crucible with concentrated sulphuric acid, the crucible covered with the convex face of a watch glass, coated on that side with bees'-wax, which has been removed again in some places by tracing lines in it with some pointed instrument,* the hollow of the glass filled with water, and the crucible gently heated for the space of half an

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* The coating with the wax may be readily effected by heating the glass cautiously, putting a bit of wax upon the convex face, and spreading the fused mass equally over it. The instrument used for tracing the exposed lines should not be too hard; a pointed piece of wood answers best. The removal of the wax coating is effected by heating the glass gently, and wiping the wax off with a cloth.

hour or an hour, the exposed lines will, upon the removal of the wax, be found etched into the glass. If the quantity of hydrofluoric acid disengaged by the sulphuric acid was very minute, the etching is often invisible upon the removal of the wax; it will, however, in such cases, reappear when the plate is breathed upon. This reappearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess."—*Fresenius.* This method cannot be adopted if the substance containing the fluorine is not decomposed by sulphuric acid, or if *silicic acid* is present: the silicic acid must be got rid of, in the way to be described, before we can discover fluorine.

396. If *nascent* hydrofluoric acid meet with silicic acid, the two compounds are mutually decomposed, FLUORIDE OF SILICON ($Si\ F_3$) and water being formed. Should the compound examined contain therefore silicic acid as well as fluorine, fluoride of silicon, and not hydrofluoric acid, will be disengaged by the sulphuric acid. Fluoride of silicon in the pure state is a colourless gas, which has a suffocating acid smell, and which emits fumes in contact with the air. It is largely soluble in water, but is thereby partially decomposed; silicic acid is deposited in the gelatinous state, and a combination of fluoride of silicon and of hydrofluoric acid is dissolved (hydrofluosilicic acid $HF,\ SiF_3$). Fluoride of silicon does not attack glass. The glass, when damp, becomes covered with a very adhesive coating of silica, which impairs the transparency of the glass, owing to the decomposition of the fluoride of silicon. It is necessary to notice the action of bases upon hydrofluosilicic acid, as the method next to be described cannot be well understood without this knowledge. Hydrofluosilicic acid combines with the basic metallic oxides, and forms with them a class of salts called silicofluorides. In order, however, to obtain these silico-fluorides, it is necessary to have the acid in excess, or at any

rate to use as much of it as is necessary to saturate the base; for when an excess of base is employed, the hydrofluosilicic acid is decomposed, the silicon separates in the form of silicic acid, and a fluoride remains in solution.

397. The method for detecting fluorine in the presence of silicic acid is founded upon the fact just stated—that when a fluoride, combined or mixed with silica, is heated with sulphuric acid, the fluorine and silicon are evolved in combination as fluoride of silicon. This method is applicable to all silicated fluorides which are *decomposable by sulphuric acid*. Boil the substance under examination with concentrated sulphuric acid in a flask, retort, or test-tube, to which is attached a bent tube; conduct the gases evolved into a solution of ammonia; heat, filter, evaporate in a platinum crucible to dryness, and examine the residue by the method described in 395. If the substance under examination contains only a slight trace of fluorine and no other volatile acid, it is better to add a very little marble to the substance, so as to ensure a continuous slight evolution of gas. When the sulphuric acid boils, all the fluoride of silicon is given off.

398. "Compounds not decomposable by sulphuric acid must first be fused with four parts of carbonate of soda and potash. The fused mass is treated with water, the solution filtered, the filtrate concentrated by evaporation, allowed to cool, transferred to a platinum or silver vessel, hydrochloric acid added to feebly acid reaction, and the fluid let stand until the carbonic acid has escaped. It is then supersaturated with ammonia, heated, filtered into a bottle, chloride of calcium added to the still hot fluid, the bottle closed, and allowed to stand at rest. If a precipitate separates after some time, it is collected on a filter, dried, and examined by the method described in 395."—*H. Rose.*

399. If a fluoride mixed with bisulphate of potash is heated in a test-tube, hydrofluoric acid is disengaged, which is easily detected by the etching of the glass.

Silicic Acid (*Silica* Si O_3).

400. The anhydrous acid is met with in two states—crystalline and uncrystalline, or amorphous. In both these states it is insoluble in water and all acids, with the exception of hydrofluoric acid. The hydrated acid is slightly soluble in water and the ordinary acids; it is rendered anhydrous and insoluble by heat. Its aqueous solution does not redden blue litmus paper or possess any taste; the presence of the acid can only be detected with certainty by evaporating the solution to dryness, and thus obtaining it in its insoluble form, as a gritty, whitish powder, which remains undissolved when the dry mass is treated with water or dilute acids; its presence should be further confirmed by testing the gritty powder with carbonate of soda before the blowpipe flame, as directed at 405. The amorphous silicic acid and the hydrate dissolve in hot aqueous solutions of the fixed caustic and carbonated alkalies, but the crystalline acid is insoluble in these reagents. The crystallized acid is, as has been stated, dissolved by hydrofluoric acid; it is also rendered soluble by fusing it with the fixed carbonated alkalies, a basic silicate being obtained, which is soluble in water, and from which acids separate it in the hydrated state. If there is sufficient water to dissolve it, when it is thus separated from basic bodies, it does not precipitate; but if there be not sufficient water present, then a portion of the acid, varying with the amount of water, precipitates, owing to its being a solid body. Silicic acid, when quite pure, is a colourless or white powder, which is more or less gritty; it is infusible and unalterable in the hottest blowpipe flame, but fuses in the flame of the oxyhydrogen blowpipe.

401. The alkaline silicates are the only salts of this acid which are soluble in water. Some of the silicates insoluble in water are dissolved with decomposition by hydrochloric or nitric acids; some of them that are not even affected by these acids when the

mixture is boiled, are decomposed by concentrated sulphuric acid. The silicates, which are not acted upon by any acids but hydrofluric acid, are decomposed by fusion with the alkaline carbonates, and also with hydrate of baryta.

402. The solution of the alkaline silicates is decomposed by all acids, even by carbonic acid. If there is not sufficient water present to dissolve the silicic acid when the silicate is decomposed, a part of it precipitates as hydrate, in the form of a gelatinous mass. If a solution of an alkaline silicate be evaporated to dryness along with a slight excess of hydrochloric or nitric acid, and if the dry mass be ignited for some little time and then treated with dilute hydrochloric or nitric acid, the other substances dissolve, whilst the whole of the silicic acid remains undissolved as a gritty powder of a whitish colour. On adding chloride of ammonium to a concentrated solution of an alkaline silicate, a gelatinous precipitate* takes place.

403. The silicates decomposable by hydrochloric or nitric acid ought to be reduced to the finest powder, before acting upon them with either of the acids; when the acid is added, the silicate must be digested in the acid, at or near the boiling point, for some time. To effect the complete separation of the silica from the bases and other acids, the acid mixture is evaporated to dryness; the silicate is thus completely decomposed : but the heat must be continued until there is no longer the least trace of acid fumes, in order to render the whole of the silicic acid insoluble ; the dry mass is then boiled with dilute hydrochloric acid. The solution containing the bases and other acids is filtered off from the insoluble silica, which is examined according to 405.

404. The decomposition of the silicates, which are not decomposable by hydrochloric or nitric acid, is best effected by fusing them with four times their weight of a mixture of carbonate of

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* Is this precipitate, which is always looked upon as hydrated silicic acid, a silicate of ammonia, corresponding to the titanate of ammonia discovered by Rose?

soda and carbonate of potash. The silicate must be reduced to the finest powder, and then intimately mixed with the alkaline carbonates, also in a state of fine powder; the mixture is then to be heated, by means of a gas lamp or Berzelius spirit lamp, in a platinum crucible, until the mixture is in a state of fusion. The crucible is then allowed to cool; and when cold or nearly so, and still containing the fused mass, it is put into an evaporating dish containing dilute hydrochloric acid. When the fused mass is detached from the crucible, remove the crucible and evaporate the mixture to dryness, and ignite just in the same way as the solution in 403 is directed to be treated. The fixed alkalies cannot of course be sought for in that portion which has been fused with the alkaline carbonates; to ascertain whether they are present, another portion of the silicate must be fused with hydrate of baryta. For this purpose " mix one part of the very finely pulverized silicate with four parts of hydrate of baryta; expose the mixture for half an hour, in a platinum crucible, to the strongest possible heat of a good Berzelius spirit lamp or to a gas lamp, and treat the fused or agglutinated mass with hydrochloric acid and water until it is dissolved. Precipitate the baryta and all the bases in the silicate, with the exception of magnesia and the alkalies, with ammonia and carbonate of ammonia; filter, evaporate to dryness, ignite, dissolve the residue in water, precipitate again with ammonia and carbonate of ammonia, filter, evaporate, ignite;" then test for potash and soda in the usual way. If the substance should contain magnesia, this will have to be got rid of by arseniate of ammonia before testing for potash and soda.

405. When silicic acid is fused with *carbonate of soda* before the blowpipe, a transparent colourless bead is formed, and carbonic acid is expelled. A small quantity of soda ought only to be employed, as an opaque bead is produced when it is added in excess.

Hydrochloric Acid (*Muriatic Acid*, H Cl.)

406. This acid is a transparent and colourless gas, of a pungent, acid, suffocating smell, and fuming strongly with moist air. It is absorbed in large proportions by water, forming the common liquid hydrochloric acid, which is a mere solution of the gas in water.

407. When a chloride is heated with *peroxide of manganese* (MnO_2) and *sulphuric acid*, chlorine gas is evolved, which may be recognized by its ODOUR and GREENISH YELLOW COLOUR.

408. When a chloride is heated with *chromate of potash* and *concentrated sulphuric acid*, a brown gas is disengaged, which condenses into a blood-red liquid, CHROMATE OF CHLORIDE OF CHROMIUM ($CrCl_3$, $2 CrO_3$). On the addition of ammonia in excess, the colour changes to a yellow, owing to the formation of neutral chromate of ammonia; upon the addition of an acid, the yellow changes to a reddish yellow colour, owing to the formation of an acid chromate.

Hydrocyanic Acid (*Prussic Acid*, H, $C_2 N$, or H Cy).

409. This acid is the hydrogen compound of the radical cyanogen ($C_2 N$), a compound composed of carbon and nitrogen.

410. In its anhydrous state hydrocyanic acid is a colourless, volatile, inflammable liquid, possessing a strong odour resembling oil of bitter almonds. Water dissolves it in all proportions: both in its concentrated and diluted state it speedily undergoes decomposition when exposed to the light. Being exceedingly poisonous, it requires to be used with care.

411. The cyanogen compounds of the metals of the alkalies and alkaline earth are soluble in water; their solutions possess an alkaline reaction, and are decomposed, with the liberation of hydrocyanic acid, by the weakest acid.

412. If, to a solution of free hydrocyanic acid or an alkaline cyanide, *potash* and a mixed solution of a *per- and proto- salt of iron* be added, a greenish blue precipitate will be produced, which,

on the addition of hydrochloric acid, will redissolve, *Prussian blue* precipitating. If only a very minute quantity of hydrocyanic acid is present, the fluid simply appears green after the addition of the hydrochloric acid, and it is only after long standing that a trifling blue precipitate separates from it.

413. If to a solution of hydrocyanic acid potash is added in excess, and then finely pulverized *peroxide of mercury*, the latter dissolves as readily as it would in free hydrocyanic acid. Since peroxide of mercury is soluble in alkaline fluids *only in presence of hydrocyanic acid*, this reaction may be looked upon as a positive test for that acid."—*Fresenius.*

414. When free hydrocyanic acid is added to sulphide of ammonium containing an excess of sulphur, the acid seizes upon some of the ammonia and sulphur, forming with them SULPHO-CYANIDE OF AMMONIUM ($NH_4 Cy S_2$), which possesses, in common with all the other soluble sulphocyanides, the property of producing with persalts of iron a *deep blood-red colour.* This test may be applied in qualitative analysis in the following way:—Add a few drops of *yellow* sulphide of ammonium to the liquid supposed to contain the hydrocyanic acid; evaporate at a *gentle heat* (not above 212 F.) until the excess of sulphide of ammonium has completely volatilized, which is ascertained by the smell; then test the solution with a drop or two of sesquichloride of iron. This test is exceedingly delicate. "If an acetate is present, the reaction takes place only upon addition of hydrochloric acid."—*Fresenius.*

415. "Neither of the above methods will serve to effect the detection of cyanogen in cyanide of mercury. To detect cyanogen in that compound, the solution is mixed with sulphide of hydrogen; sulphide of mercury precipitates; the solution then contains free hydrocyanic acid." Examine the solution, after the precipitation of the mercury, for hydrocyanic acid, either by the method described in 412 or 414.

Hydrobromic Acid (H Br).

416. Hydrobromic acid is a gas which resembles very closely in its properties hydrochloric acid gas. It emits in the air white fumes, which are denser than those produced by hydrochloric acid gas. It is decomposed by chlorine, bromine being set free, and hydrochloric acid formed: the liberated bromine appears under the form of reddish vapours; or if in more considerable proportions, it condenses into drops of a similar colour. Hydrobromic acid gas is extremely soluble in water; the solution is colourless, and, both in the concentrated or in the dilute state, it very much resembles concentrated or dilute hydrochloric acid. When, however, hydrobromic acid gas contains any free bromine, which it dissolves in large quantities, the liquid acid has a dark reddish colour.

417. Bromides are decomposed by chlorine, by nitric acid, and by concentrated sulphuric acid with the liberation of bromine, which communicates to the liquid a yellowish red colour. Bromine is soluble in ether, and imparts an orange colour to starch paste.

418. To detect bromine in any compound, add an *aqueous* solution of chlorine gas; the bromine, being set free, will communicate a yellowish red tint to the liquid, unless the quantity be very minute: an excess of chlorine should be avoided, since it converts the bromine into the colourless chloride of bromine. If the solution be now agitated with *ether*, it will remove all the bromine from the liquid dissolving it, producing a yellow-coloured solution. If the ethereal solution, which has been carefully decanted or removed by a pipette, be agitated with potash, the colour will disappear, bromide of potassium and bromate of potash being formed. By evaporating this solution to dryness, and igniting the residue, the bromate of potash will be converted into bromide of potassium. On heating the bromide along with *peroxide of manganese* and *sulphuric acid* in a small retort, YEL-LOWISH RED VAPOURS will be evolved, unless the quantity be very

minute.   These vapours, when brought in contact with *starch paste*, will communicate to it an ORANGE-YELLOW COLOUR, which disappears on exposure to the air.

419. Solid bromides, when distilled with BICHROMATE OF POTASH and CONCENTRATED SULPHURIC ACID, yield pure *bromine*, which becomes colourless, or nearly so, when treated with excess of ammonia; by this means it is distinguished from chlorochromic acid, which it resembles in colour.

HYDRIODIC ACID ($H I$).

420. This acid and its compounds resemble in their properties the corresponding compounds of chlorine and bromine.   The pure acid is gaseous.   It is extremely soluble in water, and the solution, which is colourless, resembles in its properties hydrochloric and hydrobromic acids; but it is more easily decomposed than the two latter compounds by the substances which have an affinity for hydrogen, and also by those substances which have an affinity for the other constituent, hydrogen being set free—as mercury, for instance.   The colourless solution turns speedily to a reddish brown when in contact with the air, owing to the formation of hydriodous acid ($H I_2$) and water.   Many of the iodides of the heavy metals are more insoluble in water than the corresponding chlorides.

421. *Protonitrate of mercury* throws down from solutions of the iodides a yellowish green precipitate of IODIDE OF MERCURY ($Hg I$).

422. *Perchloride of mercury* throws down a red precipitate of PERIODIDE OF MERCURY ($Hg I_2$), which is soluble in an excess of the perchloride or of iodide of potassium.

423. *Soluble salts of lead* precipitate an orange-yellow precipitate of IODIDE OF LEAD ($Pb I$).

424. Iodine, in a free state, forms with *starch*, even in highly dilute solutions, a purple precipitate of IODIDE OF STARCH.   If

the iodine is in a state of combination with hydrogen or any metal, it is necessary to liberate it before applying the starch test.

425. *Nitric acid* liberates iodine from its hydrogen and metallic compounds, nitric oxide being given off. The liberated iodine communicates a brownish yellow tint to the solution; and if it is concentrated, a portion of the iodine separates as a black precipitate. When solid iodides are heated with nitric acid, the iodine sublimes in the form of violet-coloured vapours, which condense upon the colder parts of the vessel as a blackish sublimate.

426. *Chlorine gas* likewise liberates iodine from its combinations; but if added in excess, they combine together, forming a colourless compound (chloride of iodine).

427. If iodides are heated with *sulphuric acid* and *peroxide of manganese*, the iodine sublimes in the form of violet-coloured vapours, which are easily recognized.

428. The best method of detecting iodine in a solution is to mix with the liquid a little starch paste, and acidify it with HCl. A solution of nitr*ite* of potash is then to be added, when, if much iodine be present, a dark blue colour will be instantly produced; if a very small quantity only—as, for instance, the two or three millionth part—then a few seconds elapse before the blue colour makes its appearance. Dr. D. Price, who invented this method, states that he has, in this way, detected the $\frac{1}{4000000}$th part of iodine dissolved in water as iodide of potassium. It is, he says, much more delicate than the other tests for iodides, as well as being free from the disadvantages to which they are more or less subject. If the experiment is made in a porcelain basin, the faintest indication of colour may be observed.

429. When a solution, containing 1 part of *sulphate of copper* and $2\frac{1}{2}$ parts of *sulphate of the protoxide of iron*, is added to a neutral or slightly alkaline solution of an iodide, a white precipitate of SUBIODIDE OF COPPER ($Cu_2 I$) is formed. The sulphate of

iron is added, to convert the sulphate of copper into a subsalt. The addition of ammonia promotes the complete precipitation of the iodine. Chlorides and bromides are not precipitated by this reagent.

NITRIC ACID (HO, NO$_5$).

430. The hydrate of nitric acid, when pure, is a colourless liquid, which fumes strongly in the air. It acts upon organic substances, destroying them quickly if concentrated; if they contain nitrogen, they are stained yellow by this acid. It oxidizes all the metals, with the exception of gold, platinum, and some of the rarer ones, being itself reduced to the state of nitric oxide (NO$_2$), which, in contact with the air, is converted into red fumes of nitrous acid (NO$_4$). All the oxides treated of in this work dissolve in this acid, with the exception of binoxide of tin and oxide of antimony.

431. All the neutral nitrates are soluble in water; a few basic salts are insoluble in that liquid. All the salts of this acid are decomposed by ignition, the alkaline nitrates yielding oxygen and nitrogen, and the rest oxygen and nitrous acid.

432. When nitrates are ignited in the presence of substances capable of oxidation, a portion of the oxygen passes over to them, whilst an inferior oxide of nitrogen is evolved. In some cases the combination is attended with a violent detonation; in others, vivid scintillations accompany the combustion.

433. To detect nitric acid in a solution, add to it one fourth of its volume of concentrated sulphuric acid, and *gently warm* the solution; a solution of a protosalt of iron must then be added, along with a few drops more of concentrated sulphuric acid, when the liquid will become of a deep brown colour, attended, most likely, with an energetic disengagement of gas: the colour, in this case, will soon disappear, for a reason presently to be named, but can readily be reinstated by a fresh addition of the solution of the protosalt of iron.   Or the solution of the protosalt of iron may be

added first to the solution of the nitrate, and then the concentrated sulphuric acid poured in, in such a way that it forms a layer at the bottom of the test-tube; in this case the deep brown colour will be produced at the contact-surface of the two liquids. The dark brown colour is owing to the formation of a compound of binoxide of nitrogen (NO_2), and the protosalt of iron when it is of a brown colour. This compound is destroyed by heat, with disengagement of the binoxide of nitrogen as gas—hence the fading of the colour. It may therefore be better for the young student to add the protosalt of iron when the solution of acid and nitrate is quite cold.

434. When nitrates are heated with *concentrated sulphuric acid*, in the presence of *copper turnings*, binoxide of nitrogen is evolved, which, in contact with the air, forms red fumes, owing to its conversion into nitrous acid. This experiment ought to be conducted in a narrow test-tube. The colour is best observed by looking into the test-tube lengthways.

435. If a mixture of a nitrate with cyanide of potassium in powder is heated upon platinum foil, a violent deflagration will ensue, owing to the sudden evolution of carbonic acid and nitrogen, produced by the oxidation of the cyanogen. Very minute quantities of nitrates may be detected in this way.

Chloric Acid (HO, ClO_5).

436. This acid, in its concentrated state, appears in the form of a yellow oily liquid, the odour of which resembles that of nitric acid. The dilute acid is colourless and inodorous.

437. All the chlorates are soluble in water. They are decomposed upon ignition, oxygen gas being given off and a metallic chloride left. When heated along with organic substances they deflagrate with far greater violence than the nitrates.

438. To detect this acid, add to a small quantity of the solid substance under examination a few drops of *concentrated sulphuric*

acid in the cold. The chlorate will be decomposed, SULPHATE OF POTASH and PERCHLORATE OF POTASH (KO, ClO_7) being formed along with a GREENISH-YELLOW-COLOURED gas (chlorous acid ClO_4), which escapes. The application of heat must be avoided; and the quantities operated upon should be small, to prevent any loud and violent explosion taking place.

439. If the solution of a chlorate is coloured light blue with some solution of indigo in sulphuric acid, a little dilute sulphuric acid added, and a solution of sulphite of soda dropped cautiously into the blue fluid, the colour of the indigo disappears immediately. The cause of this equally characteristic and delicate reaction is, that the sulphurous acid deprives the chloric acid of its oxygen, and the liberated chlorine discolourizes the indigo.—*Fresenius.*

440. Upon heating chlorates with hydrochloric acid, the constituents of the two acids decompose, forming water, chlorine, and bichlorate of chlorous acid (ClO_3, $2\ ClO_5$). The test-tube in which the experiment is made becomes filled in this process with a greenish yellow gas, of a very disagreeable odour, resembling that of chlorine; the hydrochloric acid acquires a greenish yellow colour.—*Fresenius.*

441. If a mixture of a chlorate and cyanide of potassium is heated upon platinum foil, a very violent deflagration ensues, even with a minute quantity of chlorate. The experiment must only be made with very minute quantities of chlorate.

ORGANIC ACIDS.

442. Organic acids cannot be detected with the same certainty and precision as the inorganic acids. To detect with certainty even some of those which we have given, requires on the part of the analyst great skill and judgment.

443. PRELIMINARY EXAMINATION.—A portion of the solid substance in powder must be heated nearly to boiling with concentrated sulphuric acid, except when chloric acid is present, as it

would be dangerous in that case to warm the solution. We will first notice the changes produced by sulphuric acid on the inorganic acids, and then on the organic acids.

444. *Inorganic Acids.*—Carbonic acid, hydrosulphuric acid, nitric acid, hydrochloric acid, and hydrofluoric acid, are evolved from the carbonates, the sulphides, the nitrates, the chlorides, and the fluorides, by concentrated sulphuric acid. The vapour of nitric acid will generally have a brown colour; the vapour of hydrofluoric acid will etch glass; and the vapour of hydrochloric acid will fume in contact with air. A greenish gas, having a smell of chlorine, will be evolved if a chlorate is present, and the solution will become yellow; vapours of bromine and iodine will be evolved if bromides and iodides are present; oxygen will be evolved if chromic acid is present, and the solution will become green; carbonic oxide will be evolved, and its presence may be proved by burning it, if cyanides or oxalates are present; it will be attended, when the latter acid is present, with carbonic acid. The other inorganic acids give off no vapours on being treated with concentrated sulphuric acid.

445. *Organic Acids.**—Tartaric, tannic, and gallic acids are immediately blackened when heated with concentrated sulphuric acid; carbonic acid is evolved at the same time from tartaric, but not from the other two. Citric and uric acids are not blackened unless boiled with the acid for some time. Benzoic, succinic, and acetic acids, are not blackened by sulphuric acid under any circumstances, but they volatilize, and in an unchanged state.

446. PREPARATION OF THE SOLUTION.—When the substance under examination is soluble in water, or if it is in solution and the fluid is water, it requires a little preparation before it can be examined with advantage for the organic acids, as it conduces much to the success of the examination if no other bases but the alkalies and alkaline earths are present. In order to remove the

* Malic acid and formic acid are not included in the course.

other bases, the solution has sometimes to be treated with sulphuretted hydrogen and sulphide of ammonium; but *generally* it is only necessary to boil the solution with a slight excess of carbonate of soda: by this reagent all the bases but the alkalies are removed. After the solution has been boiled for some time, it is filtered, and to the filtrate is added nitric acid very slightly in excess: the solution is then gently heated in order to expel the carbonic acid. After this, ammonia is added in very slight excess; and when it is required to have the solution perfectly neutral, as in testing with nitrate of silver and sesquichloride of iron, the solution, which has been rendered slightly alkaline with ammonia, is boiled in an evaporating dish until it is neutral to test-paper. When salts of ammonia are present in the substance under examination, the solution must, supposing no other bases but the alkalies are present, be boiled with carbonate of soda until all the ammonia is expelled, and the solution is then rendered neutral in the way just stated.

447. If the substance under examination is insoluble in water, but soluble in acids; or if it is a solution, and the fluid is an acid —the dry substance or the solution, whichever it may be—is boiled with a strong solution of carbonate of soda, then filtered; and the filtrate, after it has been neutralized in the way described in 446, is examined for the acids.

SPECIAL TESTS FOR THE ORGANIC ACIDS.

448. Tartaric Acid.—When this acid has been indicated by the general reagent, a special test may be made for it by adding to a neutral solution acetate, or some other salt, of potash, and then agitating the liquid very much, and allowing time for the formation of the insoluble bitartrate of potash.

449. Citric Acid.—This acid is best ascertained by the way described at 464.

450. BENZOIC ACID.—This acid, in the presence of succinic acid, is best detected by the method described at 471.

451. SUCCINIC ACID.—This acid is best detected, in the presence of benzoic acid, by the method described at 476.

452. GALLIC ACID.—This acid is best detected, in the presence of tannic acid, by the method described at 483.

453. TANNIC ACID.—This acid is best detected, in the presence of gallic acid, by the method described at 479.

454. ACETIC ACID.—This acid is detected in the way described at 488.

455. URIC ACID.—This acid is detected in the way described at 495.

TARTARIC ACID (2 HO, C_8 H_4 O_{10} or 2 HO, $\overline{T}$).

456. Tartaric acid occurs in the form of large colourless prisms, which are soluble in water, and have an agreeable acid taste; if the solution is kept a short time it undergoes decomposition.

457. Tartaric acid and its salts (the tartrates), when heated, char, and emit during the process a peculiar and very characteristic odour, resembling that of burnt sugar, which is best perceived when the substance is heated in a test-tube open at both ends.

458. *Chloride of barium* produces in solutions of the tartrates a white precipitate of TARTRATE OF BARYTA, which is soluble in solutions containing ammoniacal salts and in hydrochloric acid.

459. *Chloride of calcium* precipitates from solutions of the tartrates a white precipitate of TARTRATE OF LIME, which is soluble in acetic acid and solutions containing ammoniacal salts. It is distinguished from phosphate of lime and borate of lime by dissolving in a cold solution of caustic potash, from which solution it is precipitated on boiling, and again redissolved as the liquid cools.

T A B L E IX.

BEHAVIOUR OF THE ORGANIC ACIDS WITH THE GENERAL REAGENTS.

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL AND SLIGHTLY AMMONIACAL SOLUTIONS BY CHLORIDE OF BARIUM.

TARTARIC ACID, CITRIC ACID.

The baryta salts of these acids are soluble in dilute hydrochloric acid.

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL AND SLIGHTLY AMMONIACAL SOLUTIONS IN THE COLD BY CHLORIDE OF CALCIUM.

TARTARIC ACID.

Tartrate of lime, like borate of lime, is soluble in chloride of ammonium; it can therefore be separated from all the other inorganic acids which give precipitates with chloride of calcium, by digesting the lime precipitate in chloride of ammonium.

ACIDS WHICH ARE PRECIPITATED ON BOILING THE SOLUTION CONTAINING THE CHLORIDE OF CALCIUM.

CITRIC ACID.

TABLE IX: *continued.*

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY NITRATE OF SILVER.

Tartaric Acid, Citric Acid, Benzoic Acid, Succinic Acid.

The silver salts of these acids are soluble in dilute nitric acid.

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY SESQUICHLORIDE OF IRON.

Benzoic Acid, Succinic Acid, Tannic Acid, Gallic Acid.

The colour of benzoate of iron is *buff;* succinate of iron, *red brown;* tannate of iron and gallate of iron, *bluish black.*

Arsenious, arsenic, and phosphoric acids give precipitates with sesquichloride of iron, but fixed organic matter interferes with the precipitation.

ACIDS WHICH ARE NOT PRECIPITATED BY ANY REAGENT.

Acetic Acid, Uric Acid.

Acetic acid imparts to solutions of sesquichloride of iron a deep red colour.

460. If tartaric acid (solid) or a tartrate be heated with concentrated sulphuric acid, the mixture acquires a black or a brownish black colour, owing to the separation of carbon, which takes place simultaneously with the evolution of carbonic oxide gas.

Citric Acid ($3 HO, C_{12} H_5 O_{11}$ or $3 HO, \overline{Ci}$).

461. This acid forms large transparent crystals, which are very soluble in water and have an agreeable acid taste; the solution decomposes on keeping.

462. Citric acid chars when heated; the charring is attended with an evolution of pungent fumes, which cannot be mistaken for those evolved by tartaric acid.

463. A solution of chloride of barium produces in solutions of the citrates a white precipitate of citrate of baryta ($3 BaO, \overline{Ci}$), which is soluble in much water, in free acids, and in ammoniacal salts.

464. A solution of chloride of calcium produces in solutions of citrates, but not in citric acid, a precipitate of citrate of lime ($3 CaO, \overline{Ci}$), which is more insoluble in hot water than cold, insoluble in potash, soluble in a cold solution of chloride of ammonium, from which it is precipitated on boiling the solution. Free citric acid must be neutralized by potash or soda before adding chloride of calcium to its solution.

465. A solution of acetate of lead, when added in excess, produces in solutions of citric acid a white precipitate of citrate of lead ($3 PbO, \overline{Ci}$), which is very sparingly soluble in ammonia, but dissolves readily in citrate of ammonia.

466. Concentrated sulphuric acid decomposes, with evolution of carbonic oxide, citric acid, both free and combined, when in the solid state; the mixture blackens only after long boiling.

Malic Acid $(2 HO, C_8 H_4 O_8 = 2 HO, \overline{M})$.

467. This acid crystallizes with great difficulty, and dilequesces rapidly when exposed to the air. It gradually decomposes, when exposed to a temperature of 230 F., into fumaric acid $(HO, C_4 HO_3)$; it is decomposed, when exposed to a temperature of 392 F., into maleic acid $(2 HO, C_8 H_2 O_6)$, which sublimes, and fumaric acid, which remains behind.

468. A solution of chloride of calcium does not produce a precipitate in solutions of the free acid or its salts until alcohol is added, when white malate of lime separates.

469. A solution of acetate of lead throws down, from a solution of the acid or its salts, a white precipitate of malate of lead $(2 PbO, \overline{M})$. If the fluid, in which the precipitate is suspended, is boiled, the precipitate fuses to a mass resembling resin melted under water. . But this reaction is only distinctly marked when the malate of lead is tolerably pure; if mixed with other lead salts, it does not present this appearance, or at least imperfectly.

470. Concentrated sulphuric acid decomposes, with evolution of carbonic oxide, malic acid, combined as well as uncombined, when in the dry state; the mixture blackens only after long boiling.

Benzoic Acid $(HO, C_{14} H_5 O_3 = HO, Bz)$.

471. The pure acid appears under the form of white scales or needles, or simply as a crystalline powder. It is only slightly soluble in cold water; on the addition of hydrochloric acid to an aqueous solution of any of its salts, it separates from the solution as a white crystalline powder. It volatilizes completely when heated, with partial decomposition. The fumes cause a peculiar irritating sensation, and provoke coughing. When heated in a test-tube open at both ends, a portion of the acid condenses upon the cool part of the tube.

472. Chloride of barium and chloride of calcium do not precipitate this acid under any circumstances.

473. Sesquichloride of iron produces in neutral solutions of this acid a precipitate of benzoate of sesquioxide of iron ($Fe_2 O_3$, 3 Bz), the colour of which is pale buff. Ammonia in excess withdraws the acid from this precipitate, hydrated sesquioxide of iron remaining.

474. Benzoic acid, when heated with concentrated sulphuric acid, volatilizes, but is not blackened.

Succinic Acid (2 HO, $C_8 H_4 O_6 = 2$ HO, $\overline{\overline{S}}$).

475. This acid is crystalline and volatile; it is readily soluble in water. It volatilizes without blackening, when heated.

476. Chloride of barium, after the addition of ammonia and alcohol, precipitates this acid.

477. Sesquichloride of iron produces, in neutral solutions of this acid, a precipitate of the succinate of the sesquioxide of iron, the colour of which is reddish brown. It is decomposed in the same manner as benzoate of iron, by ammonia.

478. It behaves like benzoic acid with concentrated sulphuric acid.

Tannic Acid (3 HO, $C_{18} H_5 O_9 = 3$ HO, $\overline{Q}t$).

479. This acid is a solid body, of a light straw colour, and not crystalline. It is very soluble in water; the solution absorbs oxygen from the air, which converts the acid into two others, gallic and ellagic. It is precipitated from concentrated solutions by dilute sulphuric and hydrochloric acid, in the form of a paste. It is also precipitated by dilute starch paste, by gelatine, and albumen.

480. This acid is completely removed from its solutions by placing in the liquid a piece of animal membrane.

481. Sesquichloride of iron produces, in solutions of tannic acid or tannates, a dark blackish blue precipitate.

482. Concentrated sulphuric acid, treated with tannic acid or tannates in the solid state, produces a dark purplish black liquid immediately, but does not evolve carbonic oxide.

GALLIC ACID $(2 \text{ HO}, C_7 \text{ HO}_3 = 2 \text{ HO}, \bar{\text{G}})$.

483. This acid crystallizes in prisms of a silky lustre, of a very pale yellow colour. It is not very soluble in cold water, but dissolves in three parts of boiling water. Its alkaline solutions, when exposed to the air, become first yellow, then green, red, brown, and finally nearly black, which is produced by the absorption of oxygen. It is not precipitated by gelatine or animal membrane. By this behaviour it may be distinguished and separated from tannic acid.

484. Sesquichloride of iron produces, in solutions of this acid and its salts, a bluish black precipitate. Salts of the protoxide of iron produce a black precipitate.

485. Concentrated sulphuric acid behaves with gallic acid much in the same way as with tannic acid.

ACETIC ACID $(\text{HO}, C_4 \text{H}_3 \text{O}_3 = \text{HO}, \bar{\text{A}})$.

486. All the salts of acetic acid are soluble; the salts of mercury and silver are the least soluble.

487. The persalts of iron impart to solutions of the acetates a blood-red colour.

488. When acetates are heated with sulphuric acid and alcohol, acetic ether is formed, which is readily distinguished by its characteristic odour.

489. Concentrated sulphuric acid occasions no blackening when heated with acetic acid or its salts; from the latter it sets the acetic acid free, which is recognized by its odour of vinegar.

FORMIC ACID $(\text{HO}, C_2 \text{HO}_3 = \text{HO}, \bar{\text{F}})$.

490. By the properties which this acid and its salts possess of

reducing the oxides of the precious metals, it is distinguished from acetic and the other acids treated of in the work. The solution to be examined for formic acid is heated with nitrate of silver; a reduction instantly takes place, carbonic acid and water being formed.

491. If formic acid, or an alkaline formiate, is heated from 140 to 158 F. with perchloride of mercury, protochloride of mercury precipitates. If the mixture is heated to 212 F., metallic mercury separates along with the protochloride.—*Fresenius.*

492. Formic acid produces a blood-red colour in solutions of the persalts of iron.

493. Concentrated sulphuric acid, when heated with formic acid or a formiate, decomposes the formic acid into carbonic oxide and water; there is therefore no blackening, however long the heat may be continued.

URIC ACID ($2\,HO$, $C_{10}H_2N_4O_4 = 2\,HO$, $\bar{U}$).

494. This acid is nearly insoluble in water and hydrochloric acid. Mineral acids separate it from its compounds in the form of a white crystalline powder. It is readily dissolved by potash.

495. Dilute nitric acid, with the aid of heat, dissolves uric acid, with effervescence; if the solution be evaporated just to dryness, and if ammonia is then added gradually in excess, a beautiful purple colour is obtained. This is a very characteristic test of the presence of uric acid.

496. On fusion with alkalies, this acid disengages ammonia; when heated alone, it evolves an odour of ammonia and hydrocyanic acid.

497. Concentrated sulphuric acid dissolves uric acid, with the aid of heat, without change; if the heat be long continued, the liquid becomes dark.

CHAPTER V.

EXAMINATION OF LIQUIDS AND SOLIDS.

PRELIMINARY EXAMINATION OF A LIQUID.

498. The student, after he has passed through the different groups of bases and acids, in the manner previously described, commences the analysis of liquids, in which he has to look for all the different substances treated of in the work, with the exception of the organic acids.*

499. Before commencing the actual analysis, it is necessary to ascertain by preliminary experiments—1, Whether there is any solid substance in solution: 2, Whether the solution is neutral, acid, or alkaline.

500. 1st. *To ascertain whether there is any solid substance in solution.*—Evaporate, by a gentle heat, a portion of the liquid to dryness, on platinum foil. If no residue remain, it is probably pure water, which will be further confirmed if it has no action upon test-paper. If a residue remain, which is completely vola-

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* The student will find it conducive to his success in many respects, if he does not engage in the detection of organic acids until he enters upon the examination of solid substances. He will, of course, in *practice*, have always first to ascertain whether organic substances are really present or absent in a solution, before he commences the actual analysis, as the presence of fixed organic matter prevents the detection of many organic substances: he will likewise, in practice, have frequently to separate, by distillation, the liquid from the solid portion of a solution, in order to be perfectly certain that the fluid is *water*, and not any other liquid. This he will ascertain by examining the distilled fluid by the smell, taste, boiling point, specific gravity, &c.

tilized when the temperature is increased, the only basic substances which can be present are ammonia, mercury, arsenic, and antimony. If the residue is not volatile, or at least not completely so, other substances besides these must be present. In both cases it is requisite to perform the next experiment.

501. 2nd. The solution is examined by well prepared test-papers, as to its neutrality, &c. Each of the three cases which may occur, and the conclusions to which they lead, are considered in the paragraphs 502, 503, and 504.

502. The solution is *neutral*. A large number of substances must therefore be absent, because the neutral salts of the greater proportion of the metals possess an acid reaction. The only salts which are neutral to test-papers are the salts of silver and manganese, and some of the salts of the alkalies and alkaline earths. The alkalies, alkaline earths, silver, and manganese, are the only basic substances, therefore, which can be present; but to distinguish still further, add to a portion of the solution carbonate of soda. If no precipitate ensue, the alkaline earths and the oxides of silver and manganese must be absent; but should a precipitate be formed, all these substances may be present.

503. The solution is *acid*. The acidity may proceed from the presence of a free acid, an acid salt, or a neutral salt having an acid reaction. To ascertain to which of these causes the acidity is due, place the end of a glass rod, moistened with a solution of carbonate of soda, into a portion of the fluid in a watch-glass. If the solution becomes turbid and remains so, it is due to the presence of a neutral salt; if it becomes clear again, the reaction is due either to an acid salt or a free acid. Carbonates and sulphides cannot be present in an acid solution.

504. The solution is *alkaline*. The alkalinity may proceed

from an alkaline carbonate, silicate, borate, or phosphate; or it may arise from the presence of a free alkali or alkaline earth, or from the cyanogen and sulphur compounds of these metals. If the alkalinity proceeds from ammonia or its carbonate, a large number of substances (those which are insoluble in these reagents) must be absent. If it is due to the presence of the fixed alkalies or their carbonates, a still larger number of substances are excluded. If it is occasioned by the sulphides of the metals of the alkalies or alkaline earths, all the metals whose sulphides are insoluble in water and alkaline sulphides must be absent.

505. After the preliminary experiments have been completed, the actual analysis must be commenced, by dividing first of all the substances into groups, and these finally into individuals, as described in the former part of this work. The basic substances are first determined in analysis. When these have been discovered, correct conclusions may be drawn as to the acids which must be absent. If, for instance, baryta was found to be present in an aqueous solution, then the acids which form with it salts insoluble in water must be absent.

506. The student should never employ the whole of the solution at his disposal, but should always reserve a portion in the event of any unforeseen accident occurring, and for confirmatory experiments.

507. If the liquid under examination contains inorganic matter in suspension,* the latter, after being separated by filtration, must be brought into solution according to the methods described under the head of solid substances. The solid and liquid portions ought in most cases to be examined separately.

* The method of preparing for analysis a solution which is thick or turbid from the presence of organic matter, is described under the head of " Solid Substances containing Organic Matter" (par. 588).

EXAMINATION OF SOLIDS.

PRELIMINARY EXAMINATION OF SOLID SUBSTANCES.

508. The substance is first examined as to its lustre, colour, odour, and whether it is crystalline or amorphous, since these will frequently afford a means of classifying the substance. Thus, a metallic lustre will indicate probably a pure metal or an alloy. A blue colour will indicate the probable presence of some salt of copper; a crystalline structure the probable presence of a salt.

509. The substance is next submitted to the different blowpipe operations described in the table and text. In these experiments, only small quantities of the substance ought to be employed; for if too much is operated upon, uncertain results are the consequence. A particle the size of a mustard seed is sufficient, and that of the flux added about the size of a hemp seed. In reductions a larger quantity may be employed, because, in that case, the more metal is produced, the more easily can its nature be ascertained. In all cases it must be reduced to the finest powder. Before entering upon the different operations, we will describe the materials to be employed for the flame of the blowpipe and the substances which are used as supports, referring the student to the article on the blowpipe (55), as to the nature and use of the flame.

510. *The flame of the blowpipe.*—When coal-gas is available, it is to be preferred, since it is perfectly free from dirt and grease, and admits of being regulated with the greatest nicety. The gas-burner ought to be of an oblong shape instead of round, the current of air being blown lengthways. When gas cannot be procured, an oil lamp or wax candle may be used. An oil lamp proper for blowpipe operations can be obtained at any of the dealers in chemical apparatus — it need not, therefore, be described; it will be sufficient to say, that it must have a broad and mode-

rately thick wick, and that on each occasion the wick must be trimmed* before employing the flame for the blowpipe experiments. The best kind of oil for the lamp is pure rape or olive oil. The flame of a wax candle is far inferior in size and intensity to that of a lamp.

511. SUPPORTS.—Various materials are used as supports for the substance during the time it is exposed to the blowpipe flame; the principal are charcoal, platinum wire and foil, and glass tubes. The kind of support is regulated by the change we wish to effect upon the substance under examination.

512. Charcoal made from light woods—as the alder, willow, and pine—is the best for blowpipe experiments. It must be well burned; it must be compact and free from crevices; it must not scintillate, smoke, or burn with flame; and it must, of course, be perfectly dry. It should be cut by a small-toothed saw into pieces about six inches in length and from one to two inches in breadth, having a flat smooth surface at right angles to the rings of growth. It is this surface which is always to be used; and a good piece of charcoal may be made to serve for repeated experiments by simply filing off the used surface, and exposing a new one after each operation. The substance to be subjected to the blowpipe flame— which, if in powder, should be previously moistened with a little water, to make it cohere—is placed in a shallow hole made in the charcoal either with a knife or with a proper charcoal borer, and the charcoal is so held that the flame may impinge upon it at an angle of about 20 degrees. As it is very difficult to get charcoal sufficiently good for blowpipe experiments, Mr. John J. Griffin has provided an elegant substitute, an account of which is given in Appendix C.

513. The following are principal operations, and the order in which they are to be performed:—1, Examination of the substance in the glass tube closed at one end; 2, In the open

* The wick must be evenly cut, and perfectly free from all extraneous fibres.

tube; 3, On charcoal; 4, In the platinum forceps; 5, With carbonate of soda; 6, With borax bead; 7, With protonitrate of cobalt.

514. EXAMINATION OF THE SUBSTANCE IN THE GLASS TUBE CLOSED AT ONE END.—The glass tubes employed ought to be made of hard German glass; they must be closed at one end, and of about $2\frac{1}{2}$ or 3 inches long, and from $\frac{1}{8}$ to $\frac{1}{4}$ inch internal diameter. The tube having been thoroughly cleaned and dried, a particle of the substance to be investigated is introduced into it and heated over a spirit or gas lamp, at first gently, and then more strongly with the blowpipe, until the glass begins to soften; for the changes, consult the table as well as the text. Some metallic oxides, when ignited, assume another (in most cases, darker) colour than they possess at common temperatures —oxide of zinc and binoxide of tin become yellow; oxide of lead, oxide of bismuth, and oxide of mercury, far darker, almost black. Some salts liquefy on ignition, and when the heat is removed again solidify—the nitrates of the alkalies and alkaline earths, for example. Salts containing water of crystallization lose it on ignition, some with intumescence (borates), others with decrepitation (chloride of sodium, &c.). If the substance is mixed with a little carbonate of soda, and heated in the tube, mercurial salts, if present, will yield a sublimate of metallic mercury (*see* par. 284). If the substance is mixed with a little dry hydrate of lime, and heated in the tube without the aid of the blowpipe, ammonia salts, if present, will yield free ammonia. If the substance is mixed with bisulphate of potash, and heated in the tube without the aid of the blowpipe, nitrous fumes will be given off, if nitric acid is present; hydrofluoric acid, if combinations of fluorine are present; iodine, if combinations of iodine are present, accompanied with an evolution of sulphurous acid.

515. In case of the nonappearance of any of these reactions, it must not be always concluded that the above-mentioned bodies are entirely absent, for sulphur and arsenic may be present in

such forms that the simple application of heat will either not
sublime them, or will expel them in combinations which afford
none of the distinctive characters of the simple bodies; moreover,
two or more of these may be present together in a substance, and
afford sublimates having mixed characters, so that the individual
elements are difficult to distinguish. Such is frequently the case
with arsenic and sulphur, which, together, form a coating on the
tube, having a metallic lustre at its lower extremity, and passing
upwards successively into black, brown, red, and finally yellow—
these colours being due to combinations of sulphur and arsenic,
which are more volatile than metallic arsenic; therefore, the
examination of a substance in the glass tube affords frequently
no positive indication of the presence of a body, but merely
intimates its probable existence, to establish which, further in-
vestigations are necessary. Such intimations are, however, of
importance, as they serve as guides in after-processes.

516. EXAMINATION IN THE OPEN TUBE. — The open tubes
ought to be about 5 or 6 inches long and about $\frac{1}{4}$ inch internal
diameter; they ought to be made of hard German glass. A
small particle of the substance, in powder, is introduced into the
tube, at about half an inch from its extremity, and gradually
heated, the tube being held in a slightly inclined position, so
that a current of air may pass fully through it. By this means
the substance is roasted, or oxidized, and various matters con-
tained in it are volatilized and pass off up the tube.

517. The roasting must be performed slowly, with a gradually
increasing temperature, and with a good current of air* passing
through the tube, otherwise unoxidized matter may be volatilized
and the mineral substance clotted and fused together. If a per-
fect roasting be required, the substance, after being heated for

* By inclining the tube more or less, we have the means of regulating the
current of air; very little passes through the tube when it is held in an hori-
zontal position, but it becomes more and more active as the tube is held more
and more vertically.

some minutes in the tube, is shaken out into an agate mortar, remixed, and roasted, and this process is repeated until fumes are no longer evolved.

518. A sublimate may be formed in the second operation, when none has been formed in the first, as oxide of bismuth will be formed when the sulphide or an alloy of bismuth (scarcely any sublimate is produced on roasting bismuth itself) is present in the substance under examination, and sulphate of lead will be formed if the sulphide of that metal is present; in like manner, arsenious acid and oxide of antimony will be formed if an arsenide or an antimonide is present. If the fumes formed have an odour of garlic, it shows the presence of arsenic. It need scarcely be observed, in conclusion, that most of the reactions produced in the former experiment are also produced in this one.

519. EXAMINATION ON CHARCOAL.—In addition to the points which require to be attended to, as pointed out in the table, it should be particularly noticed whether the substance disengages a peculiar odour, as arsenic and sulphur might be detected by the odours they produce: and it should also be noticed whether the substance fuses; the oxides and acids which fuse are the oxides of antimony, bismuth, lead, and oxide of copper. "Most metallic sulphurets fuse when heated before the blowpipe upon charcoal, and this effect often takes place with sulphurets of metals the oxides of which are infusible; but many of these sulphurets become rapidly oxidized during the operation, and exhale an odour of sulphurous acid in the same way as when heated in the open tube, and are thus converted into metallic oxides. Most metals fuse before the flame of the blowpipe; and all of them, except those called noble, are subsequently oxidized by the exterior flame."

520. After this examination is complete, the substance must still be retained on the charcoal for the examination with proto-nitrate of cobalt.

521. EXAMINATION WITH CARBONATE OF SODA ON CHARCOAL.—

The substance (in powder) under examination is mixed with an equal quantity of carbonate of soda, and the mixture is made into a paste with a drop of water. After it has been dried at a moderate heat, it is exposed on the charcoal to the reducing flame of the blowpipe, the oxidizing flame spreading over the charcoal. Should no reduced metal make its appearance, after exposure for two or three minutes to the flame, a little cyanide of potassium may be added, and the experiment continued for two or three minutes longer. Many of the metallic arsenides and sulphides require to be carefully roasted, and thus deprived of their arsenic and sulphur, and the metals themselves oxidized, before they can be reduced by carbonate of soda; in this case the residue which remains from the open-tube experiment can be employed. It must be remembered, however, that cadmium as well as sulphur and arsenic may have been expelled by the roasting.

522. The metals which can be reduced by this means, besides gold, platinum, and silver, are lead, antimony, tin, copper, zinc, bismuth, nickel, cobalt, iron, cadmium, arsenic, and mercury. "Gold, silver, copper and tin, compounds, yield metallic beads, but no incrustations; iron, nickel, cobalt and platinum, compounds, give neither beads nor incrustations; bismuth, lead, and cadmium, compounds, produce a yellow or brown deposit on the charcoal; antimony and zinc give a white incrustation;* arsenic may easily be recognized by its odour."

523. If a globule has been obtained, it is necessary to ascertain whether it is malleable or brittle: "for this purpose it is allowed to cool perfectly, and carefully removed with a pair of tweezers. Having been placed upon the anvil, and struck with the hammer —or, if these two blowpipe instruments are not at hand, upon the bottom of a strong mortar—and struck sharply with the pestle, when, if brittle, it of course falls to powder (as in the case of antimony); if semi-malleable, it flattens out, at the same time

* It must be remembered that charcoal becomes, on exposure to the blow-pipe flame, covered with a *bluish white ash.*

breaking into several pieces (as with bismuth); and if fully malleable, flattens out without breaking (like lead).

524. "*The globule obtained is malleable.*—Lead (makes a black streak upon paper); a yellow incrustation is formed upon the charcoal. Tin; a slight white incrustation. Copper (known by its colour). Silver.

525. "*The globule is semi-malleable.*—Bismuth; a yellow incrustation.

526. "*The globule is brittle.*—Antimony; abundant white incrustation.

527. "*If no metallic globule* is obtained, but shining *metallic spangles* are observed after levigation; probably tin, antimony, or copper."

528. If the substance fuses into a transparent glass with the carbonate of soda, it shows the presence of silicic acid (405).

529. EXAMINATION IN THE PLATINUM FORCEPS. — "If the operator has convinced himself by a preliminary experiment that the substance under examination does not, when heated, attack platinum,* a small splinter of it is to be taken between the platinum forceps, and subjected to the oxidizing flame; but if the substance is very fusible, a piece of platinum wire, hooked at one end, may be used instead of the forceps. If, however, the substance be one which exerts a chemical action on platinum, and would therefore injure the forceps or wire, charcoal must be employed as the support. In this examination, not only the relative fusibility of a substance is ascertained, but also a knowledge of the absence or presence of certain bodies which tinge the blue oxidizing flame, of various characteristic colours, is also arrived at." To obtain the colour, the substance ought to be exposed on platinum wire to the inner blowpipe flame, and the experiment ought to be made with a very small flame and in a dark room.

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* Platinum cannot be employed when compounds of the easily reducible metals, as silver and lead, are present.

BLUE FLAMES.

Intense blue	Chloride of copper.
Pale clear blue	Lead.
Light blue	Arsenic.
Greenish blue	Antimony.
Blue mixed with green . .	Bromide of copper.

GREEN FLAMES.

Very dark green, feeble . .	Ammonia.
Dark green	Boracic acid.
Dark green . . .	Iron wire.
Full green	Copper.
Intense emerald green . .	Iodide of copper.
Emerald green, mixed with blue .	Bromide of copper.
Pale green	Phosphoric acid.
Very pale apple green . .	Barytes.
Intense whitish green . .	Zinc.

YELLOW FLAMES.

Yellow	Soda.
Feeble brownish yellow . .	Water.

RED FLAMES.

Intense crimson . . .	Strontia.
Reddish purple . . .	Lime.
Violet	Potash.

530. If the substance, on exposure to the flame, should give no characteristic colour, it ought to be moistened with dilute hydrochloric acid, and again exposed to the inner flame.

531. "In order to test the fusibility of a mineral, a small splinter having a sharp edge or point should be broken off and held in the forceps at a short distance beyond the point of the inner blue flame, so that the sharp edge is strongly heated. If a gas flame be employed, the mineral must be held somewhat further from

the point of the blue flame than is necessary in the case of an oil lamp, in order to prevent any reduction taking place which would materially interfere with the results. If a powdered substance is to be tested, or one which decrepitates when heated, and which must therefore be previously pulverized, the following process may be resorted to:—A small quantity of the powder is made into a paste with water, and spread upon a piece of charcoal; it is then dried, and strongly heated with an oxidizing flame; it will then (generally) cohere sufficiently to allow of its being taken up between the forceps and tested in the usual manner. Care must be taken that the substance, if a fusible one and one which acts upon platinum, does not fuse upon the platinum points of the forceps.

532. "If a substance be infusible, or only very slightly fusible, in the oxidizing flame, it may afterwards be submitted to the extremity of the reducing flame, since many substances infusible in the former become fusible on undergoing a partial reduction: such are the silicates of peroxide of iron, which are infusible in the oxidizing flame, but which, when converted into the magnetic silicates, fuse with more or less ease.

533. "According to their relative fusibility, minerals may be classified as follows:—

      I. Readily fusible to a bead.
     II. With difficulty fusible to a bead.
   III. Readily fusible on the edges.
   IV. With difficulty fusible on the edges.
    V. Infusible.

534. "In testing the fusibility of a mineral substance, it should be noticed whether, if fusible, a clear or opaque bead is obtained; also, whether the substance changes colour, becomes magnetic, or exhibits any phenomena of intumescence, ebullition, &c., all of which are useful characters in indicating the nature of the mineral" (*see* Appendix D).

535. " Of the metallic oxides, the following only are fusible in the oxidizing flame, viz.—the oxides of copper, lead, antimony, and bismuth. Metallic sulphides are, with few exceptions, readily fusible under the blowpipe flame : these exceptions are sulphide of zinc and sulphide of manganese."

536. TREATMENT WITH BORAX.—To obtain a bead of borax, one end of the platinum wire is bent into a small hook. This is heated in the blowpipe flame, and then dipped into the borax: a small portion of the borax will adhere to it; and this being fused in the flame, and, while hot, dipped again into the powdered borax, a fresh quantity will adhere, which is fused as before; and this is continued until a bead of the requisite size is obtained. A great many metallic oxides dissolve in borax, forming coloured glasses. If any metallic arsenides or sulphides are present, it is necessary to roast the substance in the way previously described (516), before making the examination with borax; and it is frequently advantageous, before roasting the powdered substance, to mix it with a little powdered charcoal, so as to prevent the formation of sulphates and arseniates.

537. While the bead of borax is still hot, it is touched with a small quantity of the powder of the substance under examination, and that which adheres is fused into it. The operator must then observe—1st, whether the substance be soluble or insoluble in borax; and, 2nd, the colour of the borax bead in (1) the oxidizing flame and (2) in the reducing flame, both in the hot and in the cold state. In performing this experiment, care must be taken not in the first instance to dissolve up too large an amount of the oxide or other substance under examination. If a small quantity afford no distinct reaction, more may be easily added. If, however, the colour of the bead be too intense to be clearly distinguished, the bead may be jerked off the wire, and that which still adheres fused up with a fresh quantity of borax, by which a paler and more transparent glass will be obtained.

TABLE VIII.

(1)—COURSE OF BLOWPIPE OPERATIONS TO WHICH SUBSTANCES
MUST BE SUBMITTED BEFORE COMMENCING THEIR ANALYSIS
IN THE HUMID WAY.

Heat the substance in a glass tube, sealed at one end, by means
of a spirit lamp.

Condenses on the cold sides of the tube .	WATER	Examine whether it has an *alkaline* or *acid* reaction; if the former, probably due to *ammonia*.
A *yellow* sublimate . . .	SULPHUR	Due either to its presence in the free state, or the partial reduction of a sulphide.
The substance *blackens* . .	ORGANIC MATTER . .	Charcoal being left.
Metals volatilized . . .	CADMIUM	Gives a yellowish red coating to charcoal, when heated on it in the open air.
	MERCURY	Condenses in liquid drops.
	ARSENIC	The interior surface of the sublimate is crystalline. The odour of garlic is evolved.
Volatile Oxides	OXIDE OF ANTIMONY . .	Sublimes without fusing.
	ARSENIOUS ACID . . .	Condenses in white crystals.
	ARSENIC ACID	Converted into arsenious acid and oxygen.
Acids and Ammonia volatilized . . .	Ascertained by their action on red and blue litmus paper.	
Volatile Salts .	AMMONIACAL SALTS . .	Volatilized unaltered, except when the alkali is in combination with the fixed acids.
	Most SALTS OF MERCURY	Yellow sublimate: iodide of mercury.
	Many CHLORIDES OF THE FIXED OXIDES.	

If the substance is completely volatile, ammonia, mercury, arsenic, and
antimony, need only be looked for.

(2)—COURSE OF BLOWPIPE OPERATIONS—*continued.*

Heat the substance in a glass tube, open at both ends, held obliquely.

White Sublimates	Ammoniacal Salts.	
	Oxide of Antimony.	
	Arsenious Acid.	
	Oxide of Bismuth	Melts into brownish yellow drops when heated.
	Mercurial Compounds.	
	Chloride of Lead	Melts readily when heated.
	Sulphate of Lead	Formed from the oxidation of the sulphide.
The substance becomes red	A Compound of Iron.	
The substance *blackens*	Oxide of Cobalt	Acid vapours evolved.
	Oxide of Copper	
	Organic Matter	Empyreumatic vapours.
Acid Vapours	Fluorides	Etching the glass.
	Sulphides	Yielding an odour of sulphurous acid.

Arsenious acid and the oxides of bismuth and antimony may have existed as such in the original substance, or they may have been formed in the operation from the oxidation of their metals or sulphides.

(3)—COURSE OF BLOWPIPE OPERATIONS—*continued.*

Expose the substance to the inner blowpipe flame, on
CHARCOAL.

If deflagration ensue, the presence of a *chlorate* or *nitrate* is
indicated.

Substances which volatilize or pass off in vapour.	*Substances which are not volatilized.*
MERCURY, ARSENIC, CADMIUM, ANTIMONY, ZINC, AMMONIA, SULPHUR, and LEAD partly.	SILVER, COPPER, BISMUTH, LEAD, TIN, GOLD, PLATINUM, COBALT, NICKEL, MANGANESE, IRON, ALUMINUM, CHROMIUM, BARIUM, STRONTIUM, CALCIUM, MAGNESIUM, SODIUM, POTASSIUM, SILICA, &c.

Colour of the different Sublimates.	Substances which yield *coloured incrustations.*	Substances which are *infusible, but become luminous.*	Substances which *fuse, or run into the charcoal.*
MERCURY, ZINC, AMMONIA, } White.	LEAD, BISMUTH, } Yellow.	ALUMINA, BARYTA, STRONTIA, LIME, and MAGNESIA, *and their salts.*	SALTS OF THE FIXED ALKALIES.
ANTIMONY, white, imparting a greenish blue colour to the flame.			
CADMIUM, red brown.			

(4)—COURSE OF BLOWPIPE OPERATIONS—*continued.*

Mix the substance with *Carbonate of Soda,* and expose the mixed mass to the inner blowpipe flame, on CHARCOAL.	Heat the substance before the blowpipe on PLATINUM WIRE, with a bead of· BORAX.	Heat the substance on CHARCOAL, with the blowpipe flame; then moisten it with a solution of PROTONITRATE OF COBALT : again strongly heat it in the *outer flame.*
Oxides and Combinations of Oxides which can be reduced to the *metallic state.*	Substances which give *coloured beads.*	

Oxide of	*Character of the Metal.*	*In the outer flame.*	
BISMUTH .	Brittle.	COPPER, COBALT,	. blue.
ANTIMONY	Brittle ; volatilizes in white fumes, yielding an incrustation.	NICKEL . . reddish. IRON . . . yellow.	
SILVER .	Malleable; very white.	MANGANESE,	Amethyst.
TIN . .	Malleable.	CHROMIUM . green.	
LEAD . .	Malleable, very.	*In the inner flame.*	
COPPER, GOLD,	Well known colours of the metals.	COPPER . . red. COBALT . . blue.	
NICKEL, COBALT, IRON,	These three are reduced, but yield no metallic beads; they are rendered magnetic, and can therefore be at once distinguished from the rest.	NICKEL . . grey. IRON . . . green. MANGANESE, . colourless. CHROMIUM . green.	

Substances which yield *coloured masses* when thus treated.

OXIDE OF ZINC,	green.
ALUMINA, SILICIC ACID, PHOSPHATES,	blue.
MAGNESIA . pink.	
BINOXIDE OF TIN,	a bluish green colour.

To discover the reduced metal, remove the fused mass from the charcoal, and grind it up in a small mortar with water; allow it to stand a minute, and then pour off the water and the suspended matter in it, and continue to repeat the process until the metal remains at the bottom of the mortar, perfectly free from charcoal, &c. If it is brittle, it will be in the state of very small spangles; if malleable, it will have adhered to the mortar or pestle, or a portion of it, whilst the rest may be in large spangles.

538. TREATMENT WITH PROTONITRATE OF COBALT.—No explanation, beyond that given in the table, is required.

539. If the substance should be metal or an alloy, the only blowpipe experiments which need be made are—1st, in the glass tube closed at one end; 2nd, as regards its malleability; and 3rd, heating a portion of the substance on charcoal in the reducing flame of the blowpipe.

540. When the student has completed the different preliminary experiments, he will be able to arrange the substance under one of the three following divisions:—

541. The solid substance under examination is neither a pure metal nor an alloy, and is destitute of organic matter.

542. The solid substance under examination is neither a pure metal nor an alloy, but contains organic matter.

543. The solid substance under examination is either a pure metal or an alloy.

544. Each of the three cases just named are separately considered under their respective heads.

545. THE SOLID SUBSTANCE UNDER EXAMINATION IS NEITHER A PURE METAL NOR AN ALLOY, AND IS DESTITUTE OF ORGANIC MATTER.

546. Before a solid can be acted upon by reagents, it must be brought into a state of solution. For this purpose it is submitted to the action of different fluids, and the one in which it dissolves is termed its solvent. The solvents employed in qualitative analysis are water, hydrochloric, nitric and nitro-hydrochloric acids. Water, when it can be employed, is always to be preferred.

547. The student must particularly guard against adding too much of the solvent, especially if it be an acid. To avoid this, he must add it in small quantities at a time, and apply heat after each addition. The substance should, before being submitted to the action of solvents, be reduced to the state of a very fine

powder, and fifteen or twenty grains employed for the analysis. The whole of the substance must, however, never be employed, but always a portion kept in case of any unforeseen accident, or for confirmatory experiments.

548. The powdered substance is boiled in ten times its amount of water. *It all dissolves.*—Make the preliminary experiments described under the head of Liquids, and then proceed with the actual analysis. *A portion remains undissolved.*—Filter a few drops of the liquid, and evaporate them to dryness on platinum foil. If a large residue remains on evaporation, the whole of the solution must be filtered, and submitted to analysis. The insoluble residue, after being well washed with boiling water, must be examined according to 549. If no residue remains on evaporating the aqueous solution, or at all events a very slight one, pour the remainder of the water off, and treat the insoluble substance according to 549.

549. The substance, which was partly or entirely insoluble in water, is boiled in concentrated hydrochloric acid.* *It all dissolves.*—Add to the solution the water which was poured off, and then proceed with the analysis. *A portion remains undissolved.*— Ascertain if anything has dissolved, by evaporating a portion of the fluid to dryness on platinum foil. Should this be the case, place the tube, with its contents, on one side, and proceed with the next experiment.

550. A fresh portion of the original substance is boiled in concentrated nitric acid. *The substance dissolves.*†—Remove as

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* If hydrochloric acid causes any effervescence, the evolved gas must be examined for carbonic, hydrosulphuric, and hydrocyanic acids, as directed under the " General Properties of the Acids."

† If the substance dissolves with the separation of a light-yellow-coloured mass of sulphur, it points out the presence of a sulphide. When nitric acid is employed as the solvent, as much of the free acid as possible ought to be removed by evaporation, before passing hydrosulphuric acid gas through the solution, as they decompose each other, the decomposition being attended with the separation of a large amount of sulphur.

much of the free acid as possible by evaporation; dilute the concentrated solution with water, and then proceed with the analysis. *It does not dissolve.*—Allow it to settle; pour off one half the acid, add a like quantity of concentrated hydrochloric acid, and again boil. If a portion still remains undissolved, return to the strong hydrochloric-acid mixture (549); filter, and examine the filtrate, if anything has passed into solution. The residue insoluble in acids, after being well washed, must be treated according to 551.

551. The usually occurring substances, which are insoluble in water and acids, are the sulphates of baryta, strontia, lime and lead, alumina, peroxide of iron, and their phosphates; the chlorides of silver and lead, fluoride of calcium, silicates, silica, and sulphur.

552. A small portion of the residue, insoluble in water and acids, is heated on a slip of platinum foil. If sulphurous acid is evolved along with the volatilization of the whole of the substance, sulphur only can be present. When other substances are present, add to another small portion a drop of sulphide of ammonium. If the colour remains white, silver, lead, and probably iron, are absent.

553. A small quantity of the dry residue, in the state of a very fine powder, is mixed with four times its weight of carbonate of soda and potash. The mixed mass is placed in a platinum crucible,* and heated over a Berzelius spirit lamp for about half an hour; or, what is still better, the platinum vessel is placed within a Hessian crucible containing a little carbonate of magnesia, and exposed to a full red heat, for the same length of time, in a furnace. The magnesia is employed to prevent the platinum from coming in contact with the Hessian crucible.

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* The compounds of the easily reduced metals, such as silver, lead, &c., must not be fused in platinum vessels, as they form alloys with that metal, which greatly injures or altogether destroys the platinum vessel: porcelain crucibles must therefore be employed in such cases.

554. On cooling, the fused mass is boiled with water, and filtered. The filtrate is to be examined for the *acids* and *alumina*, the residue for the *bases*.

555. *Examination of the filtrate.*—To one portion of the filtrate add hydrochloric acid until the solution is distinctly acid; evaporate to dryness, and ignite until acid fumes are no longer evolved. To the dried mass add dilute hydrochloric acid, and boil; if a residue remains, silicic acid is present. To the filtrate from the silica add ammonia in excess, and then warm the solution; if a precipitate is formed, it must be due either to alumina or its phosphate. After having filtered and washed the precipitate, examine it for alumina and phosphate of alumina according to table V. In the filtrate from the alumina precipitate, or in the solution which has failed to give a precipitate, test for phosphoric acid by adding chloride of ammonium, and then sulphate of magnesia. Acidulate another portion of the original filtrate with hydrochloric acid, and examine for sulphuric acid by adding chloride of barium. Another portion must be acidulated with nitric acid, and tested for chlorine by nitrate of silver. To detect fluorine, an examination must be made according to 397 or 398.

556. *Examination of the residue.*—After having removed all the substances soluble in water, by repeated washings, dissolve the residue, if lead and silver are absent, in hydrochloric acid, and proceed with the analysis in the usual way. If the residue does not completely dissolve in the acid, and the two metals just named are absent, it shows that a portion of the substance has not been decomposed. When this is the case, filter off, and examine the filtrate.

557. When the fixed alkalies are to be looked for in the insoluble residue, another portion, in fine powder, must be mixed with about four times its weight of carbonate of baryta, and fused in a platinum crucible, in the manner already described.

On cooling, the fused mass is digested with dilute hydrochloric acid, and filtered. The filtrate is evaporated to dryness, and ignited; the dry residue must be treated with water, and again filtered. The filtrate, after being freed from iron, alumina, baryta, lime, and magnesia, must be evaporated to dryness, to expel the ammoniacal salts which have been employed in their precipitation; if a residue remains, it must be examined for potash and soda.

588. THE SOLID SUBSTANCE UNDER EXAMINATION IS NEITHER A PURE METAL NOR AN ALLOY, BUT CONTAINS ORGANIC MATTER.

559. The presence of fixed organic matter* interferes with the detection of many substances. Thus, in the presence of tartaric acid, which is a fixed organic acid, the oxides of aluminum, chromium, and iron, and many other metallic oxides, are not precipitated by the alkalies. When an inorganic analysis has therefore to be performed upon a substance containing organic matter, this last must generally be destroyed before the examination is attempted. In most cases, this may be accomplished by simply igniting the substance in a porcelain or platinum crucible until all the organic matter has been destroyed, and afterwards dissolving the residue in water or acids. The solution must then be examined in the regular way. A separate examination must always be made in an undecomposed portion, for the salts of ammonia, mercury, arsenic, and antimony, as these substances might be entirely volatilized by the heat employed to destroy the organic matter.

560. Sometimes we are obliged to have recourse to the following method for destroying the organic matter, especially in the case of solutions which have to be examined for *poisons:*—The solid substance or solution is boiled with concentrated hydrochloric acid, to which chlorate of potash, in powder, is added

* Organic substances are termed *fixed* when they cannot be distilled or volatilized without decomposition.

gradually until the mixture becomes perfectly fluid; the solution is then heated until all free chlorine is evolved, after which it is diluted with water and filtered. The filtrate must be examined in the regular way. The residue must be examined for chloride of silver.

561. THE SUBSTANCE UNDER EXAMINATION IS A PURE METAL OR AN ALLOY.

562. Nitric acid behaves with metals in the following manner:—Gold and platinum are neither dissolved nor altered in the least degree by it. Tin and antimony are converted by nitric acid into oxides, which do not dissolve in or combine with an excess of the acid. The other metals are oxidized and converted by it into soluble nitrates. On account of the different behaviour, therefore, which nitric acid exhibits with the metals, it is usual to employ it as the solvent of alloys, &c.

563. To the metal or alloy under examination, which is placed in a small flask, is added concentrated nitric acid, and heat applied. One of the three following cases will then occur:—1. Complete solution takes place. 2. A white insoluble substance separates. 3. A metallic residue remains. Each of the three cases are considered separately in detail.

564. 1. *If complete solution ensues*, GOLD, PLATINUM,* TIN, and ANTIMONY† must be absent. After removing the greater part of the free acid by evaporation, dilute the solution with water,‡ and proceed with the analysis in the regular way. Mercury, if present, will be found in the state of peroxide.

565. 2. *If a white insoluble substance separates*, TIN and ANTIMONY are indicated. After removing the greater part of the

* Alloys of silver and platinum, with the latter metal present in small proportion only, dissolve in nitric acid.

† Very minute traces of antimony are often completely dissolved by nitric acid.

‡ If the solution becomes turbid, on the addition of water, it indicates the presence of bismuth.

free acid by evaporation, dilute the solution with water, filter, and
proceed with the filtrate in the ordinary way. The precipitate,
after being well washed with water, is treated with a hot con-
centrated solution of tartaric acid. If it all dissolves, TIN is
absent. The presence of ANTIMONY is confirmed by hydro-
sulphuric acid producing in the tartaric acid solution, to which
hydrochloric acid has been added, an orange-red precipitate. If
the whole of the *insoluble substance* does not dissolve in tartaric
acid, the solution is filtered. The filtrate is examined for anti-
mony by the method just stated. The residue, after being well
washed, is mixed with carbonate of soda and cyanide of potassium,
and exposed on a charcoal support to the inner blowpipe flame.
If tin is present, ductile metallic grains will be obtained.

566. 3. *If a metallic residue remains*, GOLD and PLATINUM
are indicated. After removing the greater part of the free acid
by evaporation, dilute the solution with water, filter, and examine
the filtrate in the usual way. The metallic residue is dissolved
in aqua regia. One portion of the solution is tested for GOLD by
means of protosulphate of iron (256). The other portion is tested
for PLATINUM by means of chloride of potassium (259).

APPENDIX.

A. The following method for the detection even of very small quantities of antimony and arsenic, in the presence of tin, has been proposed by Ansell :—The sulphides, precipitated from their solutions in alkalies or alkaline sulphides, are dissolved in nitro-hydrochloric acid, and the solution, thus obtained, poured into a hydrogen-apparatus so arranged as to allow the gas to be washed with a dilute solution of acetate of lead which absorbs any hydrochloric acid or sulphuretted hydrogen, and to pass the mixture of antimonide, arsenide, and free hydrogen, into a test-tube half filled with concentrated nitric acid, which converts the antimony and arsenic into antimonic, arsenious, and arsenic acids; the gas ought to be passed through the acid moderately slow. The nitric acid solution obtained after the gaseous mixture has passed for about a quarter of an hour, is evaporated; and the residue, after being exposed to a tolerable heat upon the sand bath, in order to expel the last traces of nitric acid, which is an essential condition of success, inasmuch as antimonic acid is slightly soluble in water containing nitric acid. The residue is now treated with warm water, which dissolves the arsenious and arsenic acids, but leaves undissolved the antimonic acid : to the solution is added nitrate of silver, and the solution is then very cautiously neutralized with ammonia, when a mixture of arsenite and arseniate of silver precipitates. The antimonic acid, which did not dissolve in the water, is dissolved in as small a quantity of nitro-hydrochloric acid as possible, and the solution evaporated as far as possible, and then tested with sulphuretted hydrogen water,

when, if any antimony is present, the liquid at once assumes an orange-yellow colour; and on boiling, decidedly orange-yellow flakes are separated. In order to detect the tin, the metallic precipitate is washed off the zinc in the generating bottle, and boiled with hydrochloric acid, when chloride of tin is formed, which may be detected by the well known reaction with chloride of mercury.

To effect the detection of small quantities of arsenic, in presence of a large quantity of antimony, the above process may be advantageously modified by passing the washed gases into a solution of nitrate of silver instead of in nitric acid; the whole of the antimony is precipitated as antimonide of silver, while every trace of arsenic remains in solution in the form of arsenious acid. On neutralizing the liberated nitric acid by ammonia, the characteristic yellow arsenite of silver is precipitated. If the gas has been passed for a long time, the solution is sometimes free from silver. In this case, the precipitate of arsenite of silver appears only after the addition of a drop of nitrate of silver. The separation of the antimony from the black precipitate, which is a mixture of metallic silver and antimonide of silver, is attended with difficulty; to detect minute quantities of antimony it is better, therefore, to follow the process first described.

B. To SEPARATE CADMIUM FROM COPPER.—The method given in the body of the Work for detecting and separating cadmium from copper is not a safe one, if only small quantities of cadmium are present; we therefore give two other methods. The neutral or acid solution is mixed with carbonate of soda until a precipitate forms; cyanide of potassium is then added, until this precipitate is redissolved; sulphuretted hydrogen is then added, the mixture heated, and, if necessary, some more cyanide of potassium added, to redissolve the sulphide of copper, which might perchance have been thrown down. The separation of the yellow sulphide of cadmium shows the presence of cadmium; the copper may be

precipitated from the filtrate by hydrochloric acid, as sulphide of copper.

Dr. Hoffmann has proposed the following method :—Acidify the solution, if it is not acid, with hydrochloric acid; then pass sulphuretted hydrogen through the solution. The two metals, if present, will be precipitated as sulphides; the precipitate must be well washed, and then boiled with dilute sulphuric acid. The sulphide of cadmium is decomposed by the sulphuric acid, sulphate of cadmium being formed, which dissolves—whilst the sulphide copper is undecomposed and undissolved. Separate the two by filtration; test the filtrate for cadmium by sulphuretted hydrogen; dissolve the sulphide of copper in nitric acid; neutralize with ammonia, acidify with acetic acid, then add ferrocyanide of potassium. This is a good method: the only precaution to be attended to is, that the mixed sulphide must be washed rapidly, so that the sulphide copper may not become oxidized by exposure to the air.

C. " The blowpipe experiments that require the assistance of charcoal may be divided into two classes. In the first class may be named the formation of beads with microcosmic salt, the trial of fusibility *per se,* and the roasting of the metallic compounds that contain such volatile elements as sulphur and arsenic. The second class of experiments is restricted to the fusion of minerals or metallic compounds with carbonate of soda, or with soda and borax, for the purpose of effecting particular combinations, or of procuring their metals in a state of regulus. For these two classes of experiments I make use of two different composition supports, the first of which I call *supports for fusions,* and the second, *supports for reductions.* They are alike in appearance. Each consists of two parts—an upper or combustible portion, and a base or incombustible portion. The former is the proper substitute for the ordinary charcoal, the under portion acting only as a crucible in which the combustible portion is contained. I shall first

describe the composition and formation of the supports, and afterwards show the way to use them.

" The incombustible portion of both supports is made of fine pipeclay and charcoal powder, mixed in equal parts by weight with as much water, slightly thickened with rice paste, as is sufficient to form a stiff plastic mass.

" The combustible portion of the *support for fusions* consists of—

Charcoal, in fine powder . 12 parts.
Rice flour . . . $\frac{1}{2}$ „
Water, about . . . 8 „

The rice is boiled in the water to form a paste, with which the charcoal is afterwards mixed into a mass of the consistency of dough.

" The upper part of the *support for reductions* consists of the following mixture:—

Charcoal, in fine powder . 9 parts.
Carbonate of soda, crystallized 2 „
Borax, crystallized . . 1 „
Rice flour . . . . $\frac{1}{2}$ „
Water, about . . . 8 „

The water is boiled, the soda and borax are dissolved in it, and the rice is then added to form a paste, with which the charcoal is finally incorporated and the whole well kneaded into a stiff mass. The mould in which these compositions are pressed to form the supports is made of boxwood.*

The principal points which require attention to ensure success in this process are to have the materials in the state of a very fine powder, and the moist compositions of a proper degree of consistency. If they are too soft, the support will not quit the

* These moulds, and every other part of the apparatus, are sold by Mr. Griffin, and, I have no doubt, can be procured through any of the other dealers in chemical apparatus.

mould without losing its form; if too dry, the particles of the support will not cohere. The proper state is found after a few trials. It is most convenient to begin by making the mixture too soft, and then drying it slowly till it is found to be hard enough to work easily. The composition is rolled into balls with the fingers. The moulds should be kept clean; and the forming parts of the pestle for the charcoal composition, and the ring, should be oiled. The point of the pestle for the clay composition must not be oiled, because grease prevents the adhesion of the combustible portion of the clay base. A pestle, made on purpose for the operation, is used to remove the finished support from the mould, by pressure on the clay foundation.

" When the support is taken from the mould, it is placed on a hot plate or sand bath to dry, after which the rough edges are taken off by a rasp. It is then ready for use. The bottoms of *supports for reductions* are painted with red ochre, mixed with rice paste, to distinguish these from the other kind. The size I have fixed upon is as follows:—height, half an inch; diameter at top, half an inch; at bottom, two fifths of an inch. The weight is about 16 grains, consisting of 10 grains of clay crucible, and 6 grains of combustible matter. I have tried several other sizes, but this I find to be the most generally convenient. Nevertheless, a higher temperature can be produced upon a smaller support; and I find that large masses of charcoal are not essential, since many blowpipe experiments can be finished during the combustion of only two grains of charcoal. When in use, they are supported by a handle made of wire, turned into the form of a ring: a piece of tobacco pipe can be used for the handle of the wire support.

" The following is the method of using these supports:—

" Firstly, the surface of one of the supports for fusion is heated before the blowpipe flame. The support continues to burn like an ordinary pastile till it is consumed down to the clay: in

K

this respect the support has a superiority over common charcoal, which soon ceases to burn when removed from the fire. The ignited support is then to be rested upon a porcelain capsule, and a quantity of microcosmic salt, sufficient to form a bead, is placed on its red-hot surface. The salt instantly melts, and sinks into the central cavity, so as to form a bead; the heat, the form, and the smoothness of the surface of the support, facilitating this part of the process. The salt is then heated before the blowpipe, till it is converted into a transparent colourless bead. The support is again placed on the porcelain capsule, and the metallic substance intended to be incorporated with the bead is added to it. The support continuing to be red hot, and the bead consequently continuing soft, the substance so added is immediately absorbed, and its loss by dispersion prevented; whereas, upon common charcoal, the fused salt solidifies soon after it is removed from the flame : and the substance added for examination, not adhering to it, is often blown away by the first blast from the blowpipe jet. The bead is now again fused, till the substance added to it is decomposed, and the resulting glass is observed to fuse quietly. It is then ready for examination; but it is sunk in the bottom of the hollow of the support, and cannot be seen by transmitted light, unless the projecting sides of the support be removed. This is effected as follows:—The support is placed, as before, on the porcelain capsule, and the operator blows with his mouth, without the blowpipe, strongly down upon its surface. The pastile then burns away rapidly, and the force of the blast disperses the ashes, until the whole rim of the support is consumed. The bead then appears situated on the summit of a cone, and can be examined either by reflected or transmitted light. It is also in a position adapted for exposure to the different action of the oxidating and reducing flames, so as to have the character of the included metal fully developed. If, finally, the charcoal is allowed to burn wholly away, the coloured

bead can be lifted from the ashes and preserved in a closed glass tube for subsequent examination and comparison.

" Secondly, if the surface of one of the *supports for reductions* be heated before the blowpipe, it becomes at first like the simple charcoal support; but in proportion as the charcoal is consumed, the fluxes which were mixed with it, and which are not volatile, concentrate and fuse upon the surface of the residue. If, there-fore, a reducible metallic compound is heated upon such a sup-port, it becomes at once exposed to the reducing action of the high temperature, of the nascent oxide of carbon, and of the carbonate of soda, whilst any earthy matter that it may contain is vitrified by the attendant borax."—*Griffin.*

D. " The degree of fusibility is a very important point to ascertain, when the examination in question refers to the native *combinations of silica* and contains other *minerals,* for this cha-racteristic feature displayed by the blowpipe is often the only one by which we may distinguish those which consist of earths, and which contain no notable quantities of metallic oxides, pro-perly so called. Amongst the minerals most frequently met with, the following are infusible :—

Quartz,
Corundum,
Tourmaline (both that which
    contains alumina, and even
    that which contains soda),
Zircon,
Cyanite,
Phenakite,
Leucite,
Talc,
Pyrophyllite,
Apatite,

Gehlenite,
Antophyllite,
Staurodite,
Refractory clays,
Hydrate of alumina,
Hydrate of magnesia,
Sulphate of alumina,
Carbonate of lime,
Carbonate of magnesia,
Carbonate of zinc,
Allophane,
Spinell,

Pleonast,
Gahnite,
Olivine,
Cerite,
Cymophane,
Gadolinite (which, being heated, becomes suddenly luminous, as if it caught fire),
Vitreous tin,
Rutile,
Titanic iron,

Tantalite,
Turquoise,
Titaniferous oxide of iron,
Chrome iron,
Native oxides of iron,
Oxide of uranium,
Tantalite,
Yttrotantalite,
Dioptase,
Chondrodite,
Topaz.

" Amongst those which are almost infusible and only become rounded at the edges, the following may be named :—

Felspar,
Albite,
Petalite,
Labradorite,
Anorthite,
Nepheline,
Tabular spar,
Pyroxène (which contains much magnesia),
Epidote (which intumesces by the first impression of the heat),
Euclase (which intumesces by the first impression of the heat),

Emerald,
Titanite,
Sodalite,
Calcareous scheelin,
Meerschaum,
Soapstone,
Serpentine,
Mica (some species, especially those found in agrnite),
Dichroite,
Heavy spar,
Celestine,
Gypsum,
Apatite,
Fluor spar.

" The following are fusible:—

Zeolites (most of them intumesce),

Spodumene (which intumesces),

Mejonite (which froths up before fusing),

Eleolite,

Amphibole (most of which boil up whilst in fusion),

Pyroxène (those which contain no excess of magnesia),

Idocrase (intumesces in fusing),

Garnet,

Cerine,

Orthite (boils in fusing),

Ferruginous scheelin,

Boracite,

Hydroboracite,

Datolite,

Botryolite,

Cryolite,

Mica (several species, especially those which contain lithia),

Tourmaline (those which contain potash),

Axinite (intumesces whilst fusing),

Amblygonite,

Lazulite,

Haüyne,

Nosian,

Eudialite,

Pyrosmalite."—*Rose's Manual of Analysis*.

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